

# **ELECTRICAL PROPERTIES AND SWITCHING IN $V_2O_5$ — $P_2O_5$ GLASSES CONTAINING METALLIC SPECIES**

**A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of**

**MASTER OF TECHNOLOGY**

*by*

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**to the**

**INTERDISCIPLINARY PROGRAM IN MATERIALS SCIENCE  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
JULY, 1976**



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# CERTIFICATE

This is to certify that this work on "Electrical Properties and Switching in  $V_2O_5$  -  $P_2O_5$  Glasses Containing Metallic Species" by Arvinda H.R. has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

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## POST GRADUATE OFFICE

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Master of Technology (M. Tech.)  
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Institute of Technology, Kanpur  
Dated: 20.7.76 21

## ACKNOWLEDGEMENT

I take pleasure in expressing the deep sense of gratitude to Dr. D. Chakravorty for his most valuable guidance and encouragement for the successful completion of this work.

I am very much thankful to Professor E.C.Subbarao and Dr. Satish C. Agarwal for their valuable advice and encouragement throughout the work.

I thank all my friends for their co-operation in the course of the work, especially Mr. Devendra Kumar for the help in the experimental work.

My sincere thanks go to Mr. B. Sharma of Ceramics Lab. for the technical help, Mr. R.N. Srivastava for typing and Mr. Ganguli for drawing the figures.

Last but not the least, I thank Mr. Vishwanath Singh for his help.

Aravinda R. Harnhalli

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## SYNOPSIS

The present work deals with the study of transport and switching properties of the vanadate glass incorporated with silver and bismuth, respectively.

The vanadate glass characteristics have been found to agree with the data reported by earlier workers.

The d.c., a.c. conductivity and optical studies on the glasses with silver and bismuth indicate a change in conductivity levels and a change in conduction mechanism from those of the base glass. A model for hopping with the metallic species has been proposed.

The a.c. conductivity and switching studies show formation of chains of metallic species. The dielectric constant increases drastically with the addition of metallic species.

The switching induced due to the metallic species in the glass matrix has been characterised for different temperatures as well as, for different mole percents of the metallic species. They reveal a strong possibility of forming reproducible threshold and memory type of switches or any combinations of them. Bismuth seems to be the proper choice for getting a stable and reproducible switch.

## CHAPTER 1

### INTRODUCTION

Amorphous semiconductors have been very widely studied ~~in the~~ recent years with renewed interests, since they have opened possibilities for fascinating device of switching and memory types, optical mass memories, negative resistance devices etc. In this age of computers and especially the energy shortage a detailed exploration of such materials may prove to be useful.

#### 1.1 Amorphous Semiconductors:

A very abstract definition of amorphous semiconductors is given by Mackenzie<sup>(1)</sup> as, "the homogeneous, single phased, and non-crystalline solid in which, (a) bulk electronic conduction at the temperature in question occurs predominantly by electrons (and/or by holes) rather than by ions, (b) the temperature coefficient of resistivity is negative."

However, one should note that heterogeneous amorphous semiconductors have also been studied in the recent years.

Classification of the amorphous semiconductors can be made according to their chemical bonding as:

Covalent non-crystalline solids

Semiconducting oxide glasses

Dielectric films

Fritzsche<sup>(2)</sup> has given a detailed discussion of all such materials. No general statements can be made on these materials, since there are many differences amongst them, just as in crystalline semiconductors. Since the present work deals with oxide glasses whatever is said in the following sections mainly concern the second group of materials.

#### 1.1.1 Electrical properties of oxide glasses<sup>(3)</sup>:

The study of electrical properties of semiconducting glasses began with the work carried out at the Leningrad school under Kolmiets<sup>(4)</sup>, on the chalcogenide glasses. They appear to behave, whether in the glassy state or liquid state, as intrinsic semiconductors with a bond gap of less than 2 ev. A very important property established by the school, which differentiates them sharply from crystalline materials of similar compositions is that their conductivity depends little on purity or stiochiometry. For them the

familiar shallow donors and acceptors of crystalline semiconductors do not seem to exist. This property has the result that the conductivity increases by many order of magnitude when they crystallise, which is certainly the reason why chalcogenide glass switches show a memory effect<sup>(4,5)</sup>

The structure of glass adjusts itself so that each atom is surrounded by a number of nearest neighbours such that all its outer electrons are taken up into bonds. Thus in chalcogenide glasses, arsenic atoms will be surrounded by three neighbours and germanium by four. In glasses with transition metal oxides the 3d electrons do not enter into bonds; transition within the d shells which absorb visible light is therefore possible.

The vanadium phosphate glasses present an interesting intermediate case, in which apparently the ( $V^{4+}$ ) ion in the state 3d' conform a bond so that the electron is tightly bound, or with the different configuration of the surroundings does not do so, so that it can hop from ( $V^{4+} \rightarrow V^{5+}$ ) sites with hardly any activation energy. Since these ( $V_2O_5 - P_2O_5$ ) vanadate glasses have been studied extensively and explained by a theoretical model of small polaron hopping, they were chosen for the present study. A detailed survey of their properties and their theoretical explanation will be given in the following sections.

## 1.2 Electronic Conduction in Vanadate Glasses:

In vanadium pentoxide crystals it has been shown<sup>(1)</sup> that the electrical conductivity increases gradually with temperature and no sharp variation in  $\sigma$  is observed when melting occurs. Whereas in regular ionic oxides like  $\text{PbO}$  a large variation in conductivity occurs abruptly at the melting temperature. So it is probable that  $\text{V}_2\text{O}_5$  glasses also show electronic conduction.

For a typical ionic solid, resistivity increases with pressure. In vanadate glasses the pressure coefficient is seen to be negative<sup>(1)</sup>. Along with these experiments, the electrolysis experiment also proves that vanadate glasses are electronically conducting materials.

The general experimental features observed by the earlier workers have been tabulated below:

- a) The d.c. conductivity of the 3d glasses varies as  $\exp(-E/kT)$  over a region 100 - 700°K. At  $T > 300^\circ\text{K}$ ,  $E$  ranges from  $\sim 0.4$  ev in the vanadate glasses to  $\sim 1.2$  ev in glasses with Ni, Co, or Cu ions<sup>(6)</sup>.
- b)  $E$  falls off with decreasing temperature in vanadate glasses from 0.4 ev to 0.05 ev. In contrast,  $E$  in the crystalline materials are constant.

- c) The conductivity mobility ( $\mu$ ) is smaller, and the activation energy is larger than in the corresponding crystal.
- d) The thermopower<sup>(7)</sup> ( $\alpha$ ) and esr signals<sup>(8)</sup> are independent of temperature for  $T > 150^\circ\text{K}$ , indicating a constant carrier concentration. The increase in  $\alpha$  for  $T < 150^\circ\text{K}$  is not reflected in the conductivity, and this resembles the behaviour of certain ferrites.
- e) The a.c. conductivity<sup>(9,10)</sup> is of the form  $\sigma \propto \omega^n$  (where  $n \approx 0.85$ ) and is independent of temperature at frequencies greater than  $10^8$  Hz. The static dielectric constant is large (20 - 40) in the vanadate glasses and increases with vanadium content<sup>(6)</sup>.
- f) Infrared<sup>(11,12)</sup>, nmr<sup>(13)</sup> and esr<sup>(8)</sup> studies show that the vanadium ion has a five-fold oxygen co-ordination, as in  $\text{V}_2\text{O}_5$ . In some of the  $\text{V}_2\text{O}_5$  pyromids, a  $\text{PO}_4$  unit probably replaces an apex oxygen, but is not clear how the  $\text{V}_2\text{O}_5$  units are linked. Phase separation<sup>(14)</sup> has been observed at high vanadium concentrations and low annealing temperatures. From these studies it was also observed that the  $\text{V}^{4+}$  site and the  $\text{V}^{5+}$  site are identical, and this explains the low activation energy for electron hopping between the two sites. The studies also indicate that valence states less than  $\text{V}^{4+}$  are unlikely.

### 1.3 Theory of Electronic Conduction:

The experimental features given in the above section along with the fact that no photo conduction exists<sup>(15)</sup> in vanadate glasses, has led various authors to suppose that semiconduction is not due to excitation of carriers but due to the thermally activated hopping amongst the vanadium ions of mixed valency.

The characteristic of vanadate glasses viz., the drop in activation energy with decreasing temperature can be explained by<sup>(16)</sup>,

- 1) Small polaronic band diffusion at low temperature and hopping at high temperature.
- 2) The hopping of a localization - induced polaron, assisted by accoustical phonons at low temperatures and optical phonons at high temperatures.

Andersons criterion<sup>(17)</sup> for the absence of diffusion requires that in order for a small polaron band to exist in the glassy state, the quantity

$$\frac{\langle E \rangle \exp S(T)}{J} \quad (1)$$

must be sufficiently small.

where  $\langle E \rangle$  - mean spread in electronic energy levels of the isolated  $\text{VO}_6^{n-}$  complexes.

$J$  - overlap integral

$S(T)$  - complex function of temperature.

Since in vanadate glasses,  $J$  is of the order of  $10^{\text{ths}}$  of  $\text{ev}^{(16)}$

$$\exp S(T) \approx 10^2,$$

$\langle E \rangle \leq 0.01 \text{ ev}$ , the quantity in the equation (1) is sufficiently small.

The general theory of small polaron conduction has been discussed in detail by Austin and Mott<sup>(18)</sup>. The present study concerns only with the application of the same to vanadate glasses.

For a polaron to be small,  $r_p$  - the radius of the polaron, must be greater than the radius of the ion on which the electron is localized, but less than the distance separating these sites ( $R_0$ ).

For a crystal

$$r_p = \frac{1}{2} \left( \frac{\pi}{6N} \right)^{1/3}, \quad (2)$$

where  $N$  - number of sites/unit volume.

Hence the polaron radius decreases as the number of sites increase. A further feature of the small polaron is the high effective mass ( $m^*$ ) of the electron inside.



The small polaron binding energy - the potential energy of the electron and that of its attendant lattice distortion for an ionic lattice is calculated to be

$$W_p = \frac{1}{2} \left( \frac{e^2}{4\pi \epsilon_p r_p} \right) = \gamma \hbar \omega_0 \quad (3)$$

ignoring the dispersion in  $\omega_0$ .

where  $\omega_0$  - optical phonon frequency

$\gamma$  - coupling constant

$\epsilon_p$  - high frequency dielectric constant.

### Small polaron theory for conductivity

#### Assumptions

- a) Conduction in vanadate glass systems is assumed to take place in the 'd' band, which is partially filled with electrons as a result of deficiency of oxygen in the structure.
- b) In the presence of ionic polarization,  $J$  - the overlap integral would be small, but because of polarization the electron phonon interaction promotes small polaron formation i.e.  $2J < W_p$ .
- c) Transport is due to non-adiabatic hopping. In which case the electron has a low chance of making the transfer

during each excitation and  $J$  can be neglected.

Condition for non-adiabatic hopping<sup>(17)</sup> being

$$J < (W_p/2kT)^{\frac{1}{4}} (\hbar \omega_0)^{\frac{1}{2}} \quad (4)$$

Low temperature behaviour suggests,  $W_D$  - the activation energy due to disorder is large and as such will effect broadening of the conduction band, as a result conduction is restricted to those states whose energy is less than  $kT$  near the fermi level. This model could be applied to any system with  $W_D$  large and  $J$  small.

### Theory

The d.c. conductivity for hopping in a degenerate electron gas is given by<sup>(18)</sup>

$$\sigma = N(E_f) e^2 R^2 p \quad (5)$$

where,  $N(E_f)$  - density of states around fermi level

$R$  - separation of sites

$p$  - jump frequency for activation by optical or accoustical phonons.

In the case of disorder the conductivity in polar materials can be split into

$$p = p(\text{opt}) + p(\text{ac}) \quad (6)$$

those due to purely optical and purely accoustical phonons respectively.

$p(\text{opt})$  is dominated at high temperatures

$p(\text{ac})$  is dominated at lower temperatures.

At some temperature  $T^{\circ}\text{K}$ , number of localized states within  $kT$  of a given state at the fermi level and within some distance  $r$ , is

$$\delta N = N(E_f) kT \frac{4}{3} \pi r^3 \quad (7)$$

Hence the energy separating one state from the other

$$W_D = kT / \delta N = \frac{P}{r^3} \quad (8)$$

where

$$P = \frac{3}{4\pi N(E_f)} \quad (9)$$

The averaging distance separating the pairs of sites

$$R = \frac{3}{4} r \quad (10)$$

$W_D$  and  $R$  can be taken to be the hopping activation energy due to disorder and the hopping distance respectively (i.e. provided  $W_D \geq 5J$ , otherwise not all states at the fermi level may be localized).

If each localized state is described by the same wave function

$$\psi = \exp(-\alpha R) \quad (11)$$

the jump frequency for non-adiabatic hopping is given by

$$p = v_{ph} \exp(-(2\alpha R + W_D/kT)) \quad (12)$$

For acoustical phonon hopping in a polaron glass this becomes

$$p(ac) = v_{ph} \exp(-(2\gamma + \frac{3}{2}\alpha r + P/r^3)/kT) \quad (13)$$

$v_{ph}$  is related to the acoustical phonon frequencies. From Mott's argument a maximum in  $p(ac)$  will occur when

$$\alpha = 2P/r^4/kT \quad (14)$$

$$\text{Hence } p(ac) = v_{ph} \exp(-(2\gamma + B/T^{\frac{1}{4}})) \quad (15)$$

$$\text{where, } B = 1.7 \left( \frac{4\pi \alpha^3 P}{3k} \right)^{\frac{1}{4}} \quad (16)$$

If the temperature dependence of  $\gamma$  and  $v_{ph}$  are ignored, from eqns. (5) and (15) we get

$$\sigma(ac) T^{\frac{1}{2}} \propto \exp(-B/T^{\frac{1}{4}}) \quad (17)$$

From Holstein's<sup>(17)</sup> proposition in crystalline materials, it was proposed that the jump frequency of  $\sigma(\text{opt})$  in the case of vanadate glasses is given by

$$p(\text{opt}) = p_0 \exp \left( - (2\alpha R + \frac{(W_D + 2W_P G)^2}{8W_P G kT}) \right) \quad (18)$$

$$\text{for } T \geq \frac{1}{4} \theta$$

where,

$$W_D = P/r^3 = \frac{kT}{\delta N} \quad (19)$$

$$G = \frac{\tanh(\hbar \omega_0 / 4kT)}{\hbar \omega_0 / 4kT} \quad (20)$$

$\theta$  is the debye temperature.

For,  $W_D$  large the  $p(\text{opt})$  maximum occurs at

$$\alpha = \left( \frac{P}{r^4} + \frac{P^2}{Qr^7(1/r_P - 4/3r)G} + \frac{2P^2}{9Qr^8(1/r_P - 4/3r)^2G} - \frac{2QG}{9r^2} \right) (kT)^{-1} \quad (21)$$

where,  $Q = e^2 / 4\pi \epsilon_P$

When the density of states is low,

$$W_P = \frac{1}{2} \left( \frac{e^2}{4\pi \epsilon_P r_P} \right)$$

and hence the last two terms of the eqn. (21) become negligible. Change in  $\sigma(\text{opt})$  should be noticeable and will take place at a temperature given by substituting  $R = R_0$  in equation (21). At higher temperatures,

$$\sigma(\text{opt}) T^{\frac{1}{2}} \propto \exp(-C/kT) \quad (22)$$

$$\text{where, } C = (W_D + 2W_P)^2/8W_P \quad (23)$$

When  $T > T_c$  the temperature dependence of  $\gamma$  should be considered. At low temperatures the factor  $G$  becomes important in the expression for  $p(\text{opt})$  making it a decreasing function.

The total activation energy is given by<sup>(15)</sup>

$$W = W_H + \frac{W_D}{2} + \frac{W_D^2}{16W_H} \quad (24)$$

#### 1.4 A.C. Conductivity and Dielectric Constants:

Consider a pair of centres at a distance  $R$  apart with energy levels differing by  $W_D$ . If  $W_D/kT \gg 1$ , the population of the upper level is  $\exp(-W_D/kT)$ . In the presence of field it is increased by  $\pm eRF/kT$ . A dipole is produced by this transfer of charge and the energy of the induced dipole in the field is

$$\frac{e^2 R^2 F^2}{kT} \exp(-W_D/kT)$$

The static dielectric constant averaging overall directions of R is

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi}{3} \frac{Ne^2 R^2}{kT} \exp(-W_D/kT) \quad (25)$$

and hence

$$\sigma(\omega) = \frac{4\pi}{3} \frac{Ne^2 R^2}{kT} \exp(-\frac{W_D}{kT}) \frac{\omega^2 \tau_0}{1 + \omega^2 \tau_0^2} \quad (26)$$

$1/\tau_0$  is the probability/unit time for a jump downwards. By the single phonon transition approximation by Miller and Abrahams<sup>(19)</sup>,  $1/\tau_0$  is independent of T and contains a tunneling factor,  $\exp(-2\alpha R)$ . When polarons are formed,  $\tau_0$  could be deduced from Schackenberg's<sup>(20)</sup> paper, the interaction being with acoustic phonons.

If we write  $\tau_0 = \tau_\infty \exp(2\alpha R)$ ;  $2\alpha R = \ln(1/\omega \tau_\infty)$ ;  $2\alpha \Delta R = 1$ , where,  $\Delta R$  is the range of values of R. One finds that the eqn. (26) predicts a variation of the form  $\sigma(\omega) \propto \omega^{0.8}$  and proportional to the temperature.

### 1.5 Optical Properties:

The small polaron theory predicts<sup>(21,22)</sup> a Gaussian-like absorption at  $h\nu = 2W_p$ . Here  $W_p$  is the

polaron binding energy, and the energy for thermal transfer ( $W_H$ ) is  $\leq 2W_P$ . Thus

$$W_{opt} \leq 4W_H \quad (27)$$

This absorption corresponds to a Frank-Condon excitation of the electron out of its polarization well. In the vanadate system it is equivalent to a charge transfer between  $V^{4+}$  and  $V^{5+}$  ions, with broadening due to disorder<sup>(22)</sup>.

For vanadate glasses it is observed<sup>(3,23)</sup> that, for  $h\nu > 2.5$  eV a steep edge occurs with a long tail extending to lower energies.

## 1.6 Switching Properties:

There are two types of switching observed in general.

(a) Threshold switching: In this case the material goes from a high resistance state (OFF state) to a low resistance state (ON state), when the applied voltage exceeds a certain value called the 'threshold voltage'. If the applied voltage is lowered below the minimum value the material reverts back to the OFF state.

(b) Memory switching: Here the low resistance state is maintained even after the zero bias is reached.



The switching mechanisms in amorphous semiconductors can be classified into three main classes as,

- (a) Electronic mechanism including thermally induced electronic breakdown,
- (b) Phase change mechanism,
- (c) Purely thermally breakdown.

A summary of which is given by Murthy<sup>(24)</sup>.

Switching in vanadate glasses:

Higgins<sup>(25)</sup> and Reegan<sup>(26)</sup> have observed threshold switching in these glasses in the temperature range  $-40^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . They found that the switching could be observed only in the glasses with  $\text{V}^{4+}/\text{V}^{5+}$  ratio in the range 10-27%. They also observed that the threshold voltage decreases with temperature and becomes zero at  $68^{\circ}\text{C}$ . The characteristics were found insensitive to additions of oxides of Li, Na, K, Mg, Ca, Sr and Ba. The switching mechanism in these glasses are believed to be due to the electronic mechanism.

#### 1.7 The $\text{V}_2\text{O}_5 - \text{P}_2\text{O}_5 - \text{RO}$ Systems:

Ioffe<sup>(27,1)</sup> studied the vanadate glasses containing  $\text{Na}_2\text{O}$  and observed that the ratio of ionic conduction contribution to the electrical conductivity is negligible even when 10.8% of  $\text{Na}_2\text{O}$  is present.

In place of RO different  $\text{VO}_x$  compounds have been introduced<sup>(12,28)</sup> and a large change in d.c. conductivity was observed. This was attributed to the change in the  $\text{V}^{4+}/\text{V}^{5+}$  ratio. A systematic survey of the effects of  $\text{WO}_3$ ,  $\text{GeO}_2$ ,  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$  and  $\text{TeO}_2$  additions upon the electrical conductivity of 80/20 vanadate glass has been made<sup>(29)</sup>. It has been reported that the glass is relatively unaffected by the replacement of oxides. It was however observed that  $\text{WO}_3 - \text{P}_2\text{O}_5$  glasses exhibited a pronounced change in d.c. conductivity with a small  $\text{V}_2\text{O}_5$  addition.

### 1.8 Glass-Metal Composites:

Metal particles are introduced into the semi-conducting glass matrix, so that the metal particles get distributed almost uniformly into the matrix. Such an introduction of metal particles could be made by several processes, like ion exchange and reduction which give surface modifications only, the other is by precipitating of particles in the matrix.

Ion exchange of the type  $\text{Na}^+ \rightarrow \text{Ag}^+$  and reduction has been tried on several oxide glasses containing bismuth oxide and their surface conductivities have been measured<sup>(30)</sup>. They show many exciting features which are not yet understood completely. These glasses have shown the electric

field induced filamentary conduction also. Such a phenomena has been shown to induce memory switching properties in the glass.

The present endeavour is to detect similar changes in the low conducting vanadate glasses. The fact that they are low conducting and easier to study makes it attractive.

## CHAPTER 2

## OBJECTIVES OF INVESTIGATION

It has been observed earlier<sup>(30)</sup> in sodium borosilicate glasses that, after ion exchange of the type ( $\text{Na}^+ \rightarrow \text{Ag}^+$ ) and reduction in hydrogen, they show memory type of switching. It has been suggested from indirect evidences, that semiconduction in these glasses arises due to electron hopping between metallic bismuth particles. As a continuation of this line of investigation, it is thought that interesting electrical behaviour can also be induced in some of the semiconducting oxide glasses. Vanadate glasses have been studied extensively to date and their transport properties have been explained by the non-adiabatic hopping of small polarons.

The objectives of the present investigation are the following,

- (1) D.C., A.C., conductivity; dielectric; and switching studies in vanadate glasses containing silver.
- (2) D.C., A.C., conductivity; dielectric; and switching studies in vanadate glasses containing bismuth.

The compositions chosen for the study are given in Table 1.

## CHAPTER 3

## EXPERIMENTAL PROCEDURES

## 3.1 Glass Preparation:

The V-O system is quite a complex one. In addition to the stable compounds,  $\text{VO}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$  and  $\text{V}_2\text{O}_5$ , having narrow homogeneity ranges, there are compounds with wide homogeneity range like,  $\text{VO}$  and magneli phases of the general formula  $\text{V}_n\text{O}_{2n-1}$  ( $4 \leq n \leq 8$ ) and  $\text{V}_n\text{O}_{2n+1}$  ( $n = 3, 4$  and  $8$ ). Several new unidentified phases also exist in the region  $\text{VO}_2 - \text{V}_2\text{O}_5$ . Oxygen forms a solid solution with metallic vanadium upto about 11 mole percent, -  $\text{VO}_{0.4}$ , distorting the cubic lattice of vanadium.

## 3.1.1 General principle of preparation:

Since vanadium pentoxide by itself is not easily rendered into vitreous state, one has to choose a multi-component system involving other oxides. Such systems should preferably give a homogeneous melt which can be supercooled to give a rapid glass. A semiconducting oxide glass may be fused with a 'network former' such as  $\text{SiO}_2$  or  $\text{P}_2\text{O}_5$ , with or without a modifier such as  $\text{Na}_2\text{O}$  or  $\text{CaO}$ . It has been shown<sup>(1)</sup> that, for all temperatures below glass transition temperature the mobility of divalent or higher

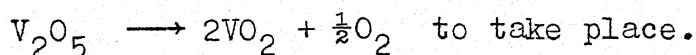
valency ions is very low for all type of oxide glasses. Further the polyvalent ions impede the motion of alkali ions which may be normal current carriers.

Vanadate glasses have been prepared with various compositions of  $V_2O_5$  ranging from 50 to 90 mole percents, by Lynch<sup>(8)</sup>, Sayer<sup>(9)</sup> and others. They observed that melting in air could form azides in the glass, and hence their preparations were done either in argon or oxygen atmosphere. They also observed that the conductivity of such materials depends very much on the  $V_2O_5$  mole percent and  $V^{4+}/V_{tot}$  ratio. So a control of stoichiometry in the glass preparation becomes important.

### 3.1.2 Control of stoichiometry

From the above discussion, and from the phase diagram of the  $VO_x$  complex, it is clear that even a slight disturbance of the oxygen state from  $x = 2.5$ , can produce other compounds of  $VO_x$ , and the short range structure in the quenched glass can change. Such variations can certainly influence the conductivity of the ultimate glass, that is obtained. Kinser<sup>(31)</sup> explained this as follows.

When say, a  $90V_2O_5 - 10P_2O_5$  glass is melted, the loss in oxygen would allow a reaction of the type



This reaction is never completed, and hence the final composition would lie somewhere between  $90\text{V}_2\text{O}_5 - 10\text{P}_2\text{O}_5$  and  $94.7\text{VO}_2 - 5.3\text{P}_2\text{O}_5$ . The result is therefore supposed to be a mixture of two vanadium oxides and phosphorous pentoxide.

The oxidation state can be controlled by passing oxygen or hydrogen into the melt.

- i) While passing oxygen, through the melt, it is necessary to control the oxygen partial pressure. For example at  $750^\circ\text{C}$  the free energy of the reaction

$\text{V}_2\text{O}_5 \rightarrow 2\text{VO}_2 + \frac{1}{2}\text{O}_2$  is 21.6 Kcal and equilibrium constant is  $2.5 \times 10^{-5}$ . Hence the nitrogen gas with oxygen partial pressure of  $5 \times 10^{-5}$  atm. would give a  $\text{V}^{4+}/\text{V}^{5+}$  ratio of 0.5, resulting in  $\text{V}^{4+}$  concentration of 15%.

- ii) While passing hydrogen through the melt, it is necessary to control the time of reaction. This is because the free energy of the reaction

$\text{V}_2\text{O}_5 + \text{H}_2 \rightarrow 2\text{VO}_2 + 2\text{H}_2\text{O}$  is (- 24 Kcal) and the equilibrium constant is  $(1.2 \times 10^5)$ .

### 3.2.3 Preparation of glass for the present work

Glasses of the composition (1)  $80\text{V}_2\text{O}_5/20\text{P}_2\text{O}_5$ , (2)  $70\text{V}_2\text{O}_5/30\text{P}_2\text{O}_5$  were prepared for a comparison of the

the measurements with the reported measurements. Since the present interest was to study the effect of the incorporation of metal particles in these glasses, no importance was given to the stoichiometry control. However, the melt temperature before quenching to the glassy state was maintained constant around 900°C.

The method of incorporating metal particles by the ion exchange and reduction on the surface were tried. A glass with  $\text{Na}_2\text{O}$  as one of the composition was prepared. This was used to get an ion exchange of the type  $\text{Na}^+ \rightleftharpoons \text{Ag}^+$  by heating in silver nitrate solution. Since the vanadate glass softening temperature is around 250°C and the silver nitrate melts only after 220°C, this method of incorporation was found unsuitable.

Glasses with silver were prepared with the addition of  $\text{Ag}_2\text{SO}_4$  in the base glass composition. The melt was maintained at 900°C for an hour and agitated thoroughly by a ceramic rod. This process precipitates silver in the glass. The melt was cast into a water cooled copper plate. The high mole percent vanadium pentoxide glasses were prone to be very brittle. They were transferred almost immediately after quenching, into an annealing furnace, where they were annealed for 24 hours at 150°C.



Glasses with bismuth were prepared by adding bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) into the base glass composition. The preparation is similar to that of the glass with silver.

All the glasses were melted in a non-porous alumina crucible and were exposed to air. They were heated slowly from room temperature to  $900^\circ\text{C}$  to avoid the loss of  $\text{P}_2\text{O}_5$  in the composition. Bulk glasses prepared as mentioned above were polished by silicon carbide particles of 250 mesh. If water is used as a medium for polishing, the glasses were found to ~~leave~~ vanadic acid. This would give rise to a possibility of change in the vanadium concentration at the surface. This in turn would give contact problems. Hence using of water was avoided during polishing, instead acetone was used. These glasses were cleaned in acetone vapours and preserved in a desiccator.

### 3.3 Preparation of Glasses in Thin Film Form:

#### 3.3.1 Blown thin films:

The viscosity of the melt in the alumina crucible was controlled by changing the temperature suitably, to make the blowing of films possible. Films were blown by a controlled passage of nitrogen through a quartz tube, which is dipped into the melt. The blowing is done

immediately after the quartz tube was removed outside the furnace, so that both quenching to room temperature and film formation takes place simultaneously. The thickness of the films blown in this way range from 10 - 100 micrometer. In very thin films non-uniform distribution was observed. With increasing thickness the films became brittle. So the optimum thickness films (25 - 50 micrometer) were used for measurements. This method of blowing films from the melt does not vary the stoichiometry of the melt. Hence this method is supposed to be very effective.

### 3.3.2 Thin films by evaporation of glass:

Although glass evaporation by sputtering of glass in argon atmosphere is supposed to be the best, the vacuum evaporation methods have been shown to give thin films similar to blown films in properties<sup>(24)</sup>. Hence a trial for the deposition of thin films of vanadate glasses was made. Tungsten and molybdenum boats were found useless, as they got corroded before the glass evaporated and no further heating was possible. The black charred material found on the surface of the boats was thought to be a compound of the respective materials with vanadium oxide. Graphite crucibles with a coating of alumina on the inner walls were found best suited

for the evaporation of vanadate glasses. The glasses evaporated had a thickness in the range of 1000 - 5000 Å. The thickness was measured by the standard interference technique which was accurate to 25 Å.

### 3.4 Electrode Properties:

It is very essential to standardise the electrodes used for glass specimens before any meaningful studies on transport properties could be carried out. We can classify the contact problems according to the different properties they exhibit.

(i) Space charge layers: When a metal is placed in contact with an amorphous semiconductor the difference in electronegativity of the materials will cause a transfer of charge until the two fermi levels of the two materials are equalised. They may come to equilibrium with a certain space charge layer formed if any surface states are present. Both the existence and the sign of the space charge can be observed by studying the barrier photovoltage, i.e. the light induced change of the resistance as a function of wavelength and the barrier capacitance.

(ii) Capacitance: Van Roosbroeck and Casey<sup>(32,33)</sup> explained recently that under certain circumstances, even ohmic conduction at low fields can be dominated entirely by space charge and contact effects. This happens in the so-called 'relaxation case', when a semiconductor whose diffusion length life time is short compared to the dielectric relaxation time, the glass is contacted by a barrier space charge current. This situation can be detected by scaling of resistance with electrode separation, and also by measurement of capacitance as a function of frequency. However capacitance measurement may be very difficult if the contact resistance is very low. The most quantitative methods would be to measure the barrier photo-voltage<sup>(34)</sup> or the thermostimulated depolarization<sup>(35)</sup>.

The low frequency parallel capacitance will be orders of magnitude higher compared to the high frequency capacitance, if a space charge polarization exists. The space charge capacitance can only be measured if the dielectric relaxation time  $\tau_{rel.} = \epsilon \epsilon_0 / \sigma$  corresponding to space charge polarization is different from that pertaining to the bulk. It is obvious from this that one expects a change in capacitance depending on the relative magnitudes of the thickness and relaxation times of the space charge region and the bulk.

(iii) Rectifying property: It has been observed in most of the amorphous semiconductors which show space charge polarization, the I-V characteristics remain linear. This is because amorphous semiconductors are intrinsic in character. However in the case of vanadate glasses with a high mole percent of  $V_2O_5$ , blocking contacts occur<sup>(8)</sup>.

It is obvious from the above discussion that a study of the; I-V characteristics, capacitance variation with frequency, change of current with time, conductivity variation with thickness of the glass, observation of barrier photovoltage and thermostimulated depolarization, reveals the different aspects of the contact problems. However from the above discussion we also note that it would be sufficient to carry out the first three experiments to assure the goodness of the contact.

(iv) Choosing of the proper contact for vanadate glasses: mentioned  
The three experiments/above were carried out for the vanadate glasses with the contact metal as (1) Ag paste, (2) Aluminium evaporated, and (3) Gold evaporated.

The study reveals that, the capacitance has a wide dispersion in the case of Ag paste and Aluminium electrode on glass 1 and 3, as shown in figs. 35, 36. In the case of Ag paste on glass 1, the capacitance value ranges from  $10 - 10^4$  FF, with aluminium electrode it

ranges from  $50 - 10^4$  PF, whereas with gold it ranges from  $3.4 - 3.6$  PF. Hence with the gold electrode the space charge polarization was thought to be minimum.

The I-V characteristic studies and current vs. time curves (fig. 34) indicated that gold acts as a non-blocking electrode. Hence gold was chosen as the contact material for the transport studies.

### 3.5 Sample Holder:

Since the phosphate glasses are prone to absorb atmospheric water vapour, all the measurements should be done in a dry atmosphere. Oxidizing or reducing atmospheres would change the oxidation state of the glass. Hence one has to do the measurements in an inert atmosphere like nitrogen. The water vapour even if present in a low percentage, could easily condense when the cell is taken to lower temperatures. To remove any such possibility one needs to evacuate the cell to maintain a low pressure dry nitrogen gas.

A measuring cell was constructed considering all these necessities. The figure 0.1 shows descriptions of the cell. The leads from the sample holders were taken through a teflon connector. The vacuum sealing of the connector was done with silicone rubber. The leads were

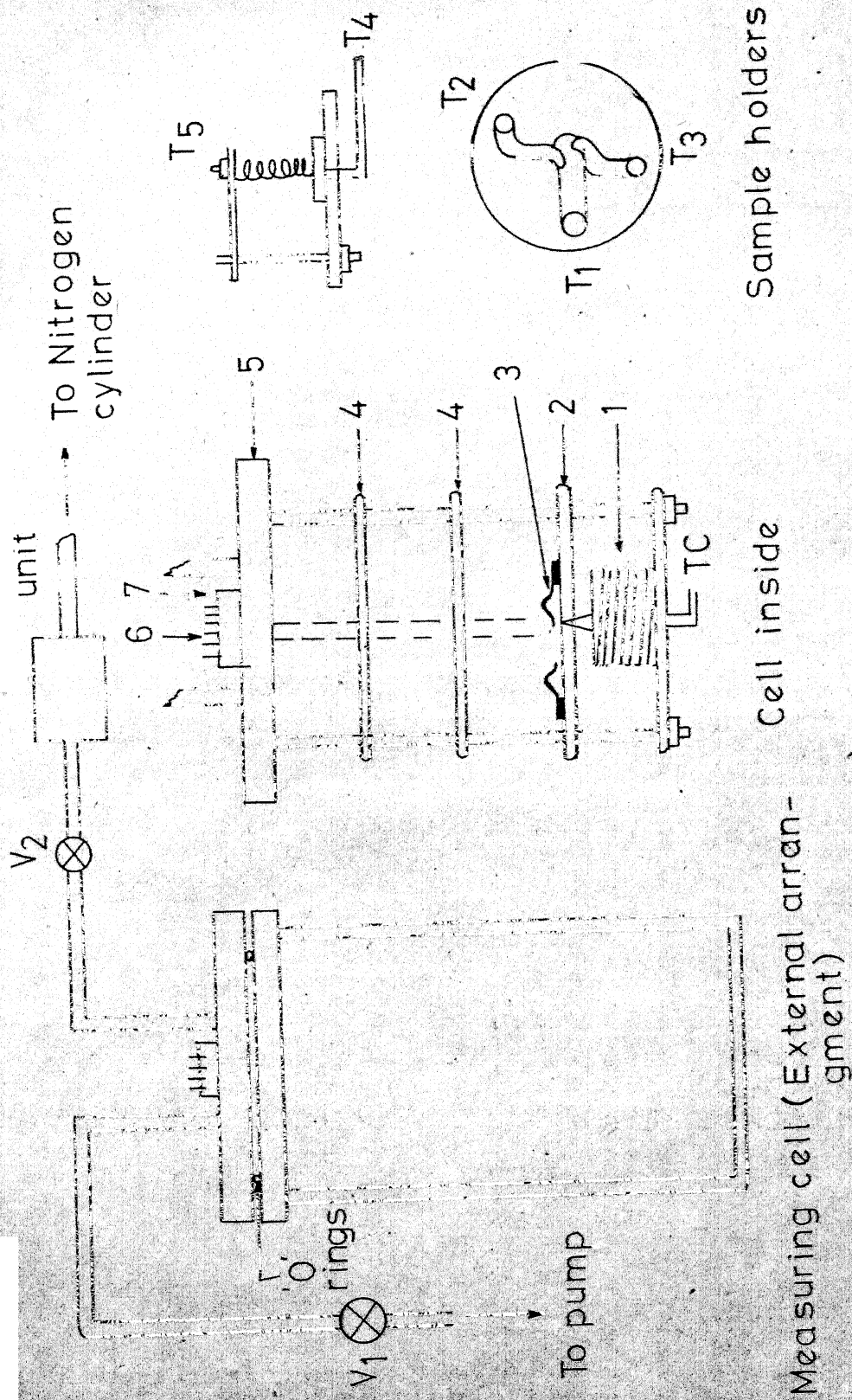
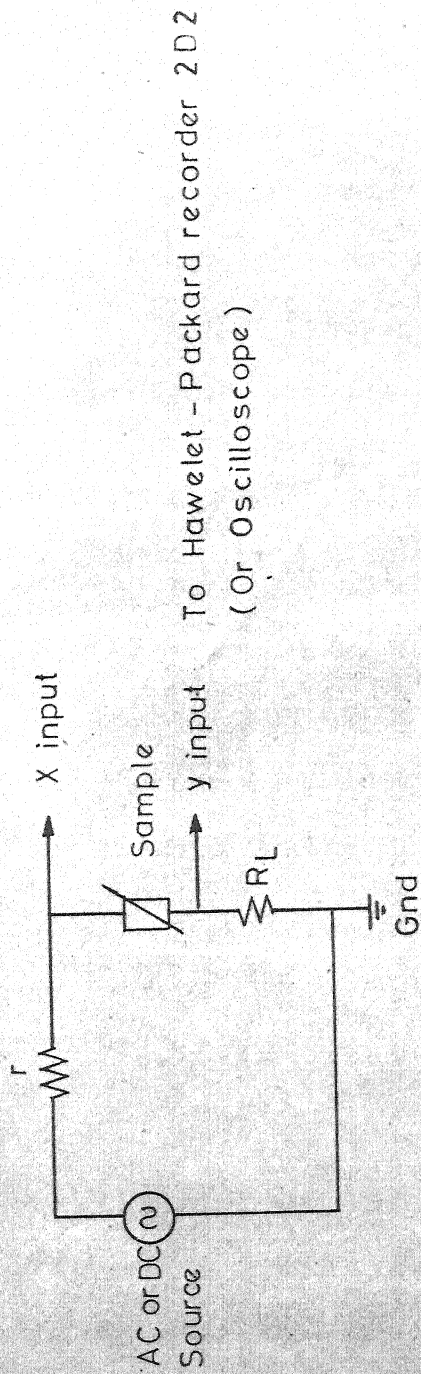


FIG. 0.1 DESCRIPTION OF MEASURING CELL.





CIRCUIT USED TO MEASURE : THE DC CONDUCTIVITY AND SWITCHING.

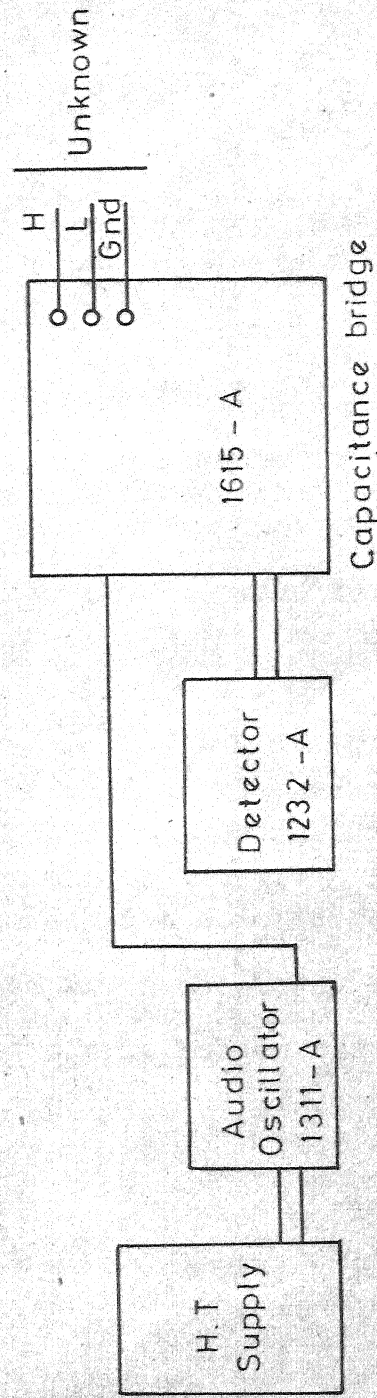


FIG. 0.2 BLOCK DIAGRAM FOR AC CONDUCTIVITY MEASUREMENTS.



shielded by copper tubes with an insulation by ceramic beads between them. The teflon connector was kept cool by passing water around it.

A sample holder (1) was made of alumina base. The sample holder had provisions for pressure contacts made of phosphor bronze strips.

Another sample holder (2) was made for measurements with thin films. This was also of alumina base, but the pressure contact was with a spring.

Capacitance and bulk conductivity measurements were done with sample holder (1). The leads from outside the teflon connector were taken with shielded cables. The connectors used were shielded BNC connectors. The total capacitance of the leads and sample holder was around 1 PF. The sample holder (2) had a resistance of five ohms, because of the spring.

### 3.5 Methods of Measurement:

#### 3.6.1 D.C. conductivity measurements:

Sufficient care was taken to choose the contact material for the glasses, as described in the Section 3.4.

For d.c. measurements to be reliable, one has to note that the voltage drop across the current measuring

device must be negligible, i.e. it should have a very small internal resistance. Impedance of the voltage measuring device must be large with respect to the specimen resistance. The circuit used is shown in the fig.0.2. In measurements of resistance when the sample resistance was less than  $10^6$  ohms, a Hawelet Packard VTVM (410 C) of internal resistance  $10^6$  ohms was used. Current measurements were done by observing the voltage drop across a minimum possible resistance. For sample resistances greater than  $10^6$  ohms, either a Electrometer (GRE 1230A) or a Digital Picoammeter (ECIL EA813A) was used. A resistance  $r$ , was used to attenuate the voltage applied. Since the current path takes the path of least resistance, care was taken to deposit electrodes, such that the top electrode is in the centre of the sample. This minimises the surface conductivity between the electrodes. For surface conductivity measurements, electrodes were deposited on one of the surfaces with a gap of 1 mm.

### 3.6.2 A.C. conductivity and dielectric measurements:

The samples were coated with gold electrodes with a gaurd ring on the top electrode. Sample holder (2) was used to make the pressure contacts for the measurement. The apparatus used for capacitance and loss measurements

are indicated in the fig. 0.2. The capacitance bridge type 1615-A was used along with the detector type 1232-A and generator type 1311-A. Three terminal binding post connection was used for the measurement. In this type of connection, the capacitor terminals were connected to the H and L binding posts and the guard ring to the GND post. The shield of the cables and outer case of the cell was also connected to the GND post. The self check for the bridge was done as mentioned in the manual. The capacitance of the shields and cables used was determined. The total capacitance of the unit without the sample was 1 PF. To make sure that the measuring methods were proper, the following experiment was conducted.

A resistance of  $10^5$  ohms and a capacitance of 86 PF were connected in parallel and plugged to the H and L binding posts. The dissipation factor (D) and the capacitance (C) measured were 0.16 and 87 PF at 100 KHz. The d.c. dissipation factor was calculated to be 0.16. This was checked at various frequencies.

Whenever the D max scale measurements were done, the a.c. conductivity (G) was calculated by

$$G = \frac{1}{R_P} = \omega C_S D \quad (28)$$

where,  $\omega = 2\pi f$ ;  $f$  = frequency in Hz;  $R_p$  = parallel resistance;  $C_s$  = series resistance;  $D$  = bridge read out multiplied by the frequency in KHz. Basic  $D$  accuracy is  $\pm (0.1\% \text{ of measured value} + 10 \text{ ppm})$  at 1 KHz, and over most of the range from 50 Hz to 10 KHz.

Whenever  $G$  Max scale was used, the a.c. conductivity can be directly read from the scale (with a multiplication factor,  $M$ , as indicated on the  $C$  Max scale). The basic  $G$  accuracy is  $\pm (1\% + 0.00001 \mu \text{ mho})$ . This is independent of frequency from 50 Hz to 10 KHz.  $D$  can be calculated from the  $G$  measured by the relation given in eqn. (28).

The dielectric constants were calculated using the following relations

$$D_1 = \text{dissipation factor} = \epsilon''/\epsilon' = (\tan\delta_{AC} - \tan\delta_{DC}) \quad (29)$$

$$D = \tan\delta_{AC} \rightarrow \text{loss measured,}$$

$$D_{DC} = \tan\delta_{DC} = 1/\omega C R_{DC} \quad (30)$$

$\epsilon''$  and  $\epsilon'$  are the imaginary and real part of the dielectric constant respectively.

$$\epsilon' = CH/\epsilon_0 A ; \quad \epsilon'' = D_1 \epsilon' \quad (31)$$

where,  $\epsilon_0 = 8.85 \times 10^{-12}$  F/m, H is the thickness of the sample in cm and A is the area of the electrodes in  $\text{cm}^2$ .

The  $\epsilon'$  and  $\epsilon''$  were rechecked by the relations,

$$\omega\epsilon_0\epsilon'' = (G_{AC} - G_{DC}) ; \quad \epsilon' = \epsilon''/D_1 \quad (32)$$

### 3.7 Characterization of the Glass:

#### 3.7.1 X-ray measurements:

X-ray spectra of both the vanadate glasses and the metal-glass composites were taken. All the glasses show very broad peaks characteristics of amorphous materials, (fig. 0.3), which were attributed to the  $V_2O_5$  compound. No specific peaks which could be attributed to silver/bismuth metallic particles or its compounds were found. This is probably because the metallic particles are less than  $100 \text{ \AA}$  in size. Chakravorthy<sup>(30)</sup> has also found similar difficulty in silver containing borosilicate glasses. He could, however, detect the silver particles by electron microscope photographs.

#### 3.7.2 Chemical analysis:

The volumetric analysis was carried out to find the total vanadium and reduced vanadium concentration.

The sample was ground well and dissolved thoroughly in water with a slight addition of concentrated sulfuric acid. This was titrated with potassium permanganate ( $\text{KMnO}_4$ ) N/10 solution. From the volume of the  $\text{KMnO}_4$  consumed, the vanadium concentration was calculated using the relation

$$1 \text{ ml of } 0.1 \text{ N } \text{KMnO}_4 \implies 0.005094 \text{ g. of vanadium}$$

This vanadium concentration corresponds to the reduced vanadium, since  $\text{KMnO}_4$  is an oxidizing agent, and the reduced vanadium would get oxidized during the titration. Since the valence states less than  $\text{V}^{4+}$  were found unlikely by esr measurements<sup>(35)</sup>, the reduced vanadium concentration was taken for  $\text{V}^{4+}$  concentration.

The oxidized solution left from the first titration was reduced completely, i.e., till all the vanadium gets reduced, using ferrous ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ . The excess was removed by adding potassium dichromate. The point of complete reduction was checked by putting a drop of the solution on  $\text{K}_3\text{FeCN}_6$  solution. This solution is again titrated with  $\text{KMnO}_4$  to give the total vanadium concentration. The concentration of  $\text{V}_2\text{O}_5$  was calculated using the relation

$$1 \text{ ml of } 0.1 \text{ N } \text{KMnO}_4 \implies 0.009094 \text{ g. } \text{V}_2\text{O}_5$$

All the titrations with  $\text{KMnO}_4$  were done in ice cold solutions. The end point was noted when the colour remains for 30 seconds. The total vanadium concentration was also checked by a gravimetric analysis<sup>(36,37)</sup>. Table 3 gives the analysis for different glasses.

### 3.7.3 Density measurements:

Dibutyl phthalate was used as a medium to find the density of vanadate glasses. The weight of the glass in air ( $W_2$ ) and the weight loss ( $W_2 - W_1$ ) in the liquid were measured, and the density was calculated using the relation

$$D_S = \frac{W_2 D_L}{(W_1 - W_2)} \quad (33)$$

Table 3 gives the density values for all the glasses.

### 3.8 Optical Measurements:

Optical absorption spectra were taken with the blown films of the vanadate glass. The absorption coefficient ( $\alpha$ ) was calculated using the relation

$$\alpha = \frac{A(\text{atomic weight of the T.M.I.})}{x \rho t} \quad (34)$$

where,  $A$  is the absorbance  $= \log I_0/I$ ;  $I$  is the transmitted intensity  $= I_0 e^{-\alpha t}$ ;  $\rho$  is the density in g/ml;  $t$  is the thickness of the specimen in cm;  $x$  is the concentration of the transition metal ion (T.M.I.) in the glass in mg/g.;

$\alpha$  is the absorption coefficient  $= \frac{4\pi k}{\lambda}$ ; and  $k$  is the extinction coefficient. The measurements were done in the range of 12,000 Å to 2,000 Å on the carry-14 instrument.



## CHAPTER 4

## EXPERIMENTAL RESULTS

## 4.1 Electrical Conductivity:

The temperature dependence of d.c. conductivity was studied in the range 100°K to 500°K. Gold coating by vacuum evaporation was done to deposit the electrodes. The pressure contacts and sample holder described earlier were used for taking measurements.

The temperature dependence was plotted as  $\log \rho$  versus  $1/T$ . The figures 1 to 7 show the temperature dependence of  $\log$  (resistivity) of the glasses 1 to 7 respectively. All the glasses show a linear temperature dependence at higher temperatures, usually above 200°K, in accordance with the eqn. (22) of Section 1.3.2. The change of slope occurs around 200°K  $\approx 1/3 \theta$  (where  $\theta = 600^\circ\text{K}$  in vanadate glasses), as was found by the earlier workers<sup>(6)</sup>. The glass no. 1 has been compared with the Sayer and Mansingh<sup>(9)</sup> curve for the same composition, in the figure 1. The agreement between the curve is satisfactory.

To find the agreement with the eqn. (17) of Chapter 1.3, the  $\log \rho$  versus  $(1/T)^{1/4}$  plots have been

drawn in the figures 1 to 7 for all glasses. All the glasses show linear dependence with a change of slope at lower temperatures, immaterial of whether the glasses contain silver or bismuth. However a two stage freezing of the conductivity was found in the 5 mole percent silver glass (no. 3) (the discussion of which is given later).

From these graphs the value of C and B were estimated. They have been listed in Table 4. In glasses as the ions are further separated than in crystals, the approximation  $W_H = \frac{1}{2} W_P$  is found to be a good one<sup>(39)</sup>. Where,  $W_H$  is the activation energy for hopping. Hence from eqn. (23) of Section 1.3, assuming  $W_D$  very small we get

$$C = W_H + \frac{1}{2} W_D = W_{\text{tot}} \quad (35)$$

So the value of C in ev gives the total activation energy at any temperature. For temperatures less than  $\theta/3$ , the multiphonon process of higher temperatures freezes to a single optical phonon process and thus the total activation energy decreases to a value with  $W_H = \hbar \omega_0$  (where,  $\omega_0$  is the optical phonon frequency). However it has been found that C at lower temperatures is very sensitive to preparation methods, annealing etc., suggesting that  $W_D$  term dominates. Hence

$$C_{\text{lowest temp.}} \approx \frac{1}{2} W_D .$$

At lower temperatures the analysis from eqn. (22) would not be proper, since the acoustic hopping dominates, as explained in Section 1.3. Hence the low temperature slope B of  $\log \rho$  versus  $(1/T)^{1/4}$  was used. Using eqns. (10), (16), (19), we get

$$B = 1.7 \left( \frac{4\pi \alpha^3 P}{3k} \right)^{1/4} = 2.4 \left( \frac{W_D (\alpha R_0)^3}{kT} \right)^{1/4} \quad (36)$$

where,  $R_0$  is the distance between the sites calculated from density

$$R_0 = \left( \frac{\text{density of glass}}{\text{density of } V_2O_5 \text{ crystals}} \right)^{1/3} (3.73 \text{ \AA})$$

Since on estimation of  $\alpha$  from the eqns. (15), (21) and (22) is very complicated, a value of  $\alpha = 2.5 \text{ \AA}^{0.1}$  was assumed (This value was suggested by Austin<sup>(3)</sup>). An estimation of the activation energy for disorder was done by eqn. (36).

Using eqns. (9) and (2) the  $N(E_F)$  - density of states around fermi level,  $r_p$  - the polaron radius, and  $a = (1/N)^{1/3}$  - the average distance between the hopping sites, were calculated. The values for the same have been tabulated in Table 5.

The values of  $W_D$  as shown in Table 5, seems to be very high ( $> kT = 0.1$  ev) in most of the cases. This was also noticed by Austin<sup>(3)</sup> in his calculations. It was suggested by him that this analysis would be true only at very low temperatures (less than 50°K). Recently the curves have been fitted to an equation of the form

$$T^n \exp(-W_D/kT) \quad (37)$$

for acoustic hoppings<sup>(40)</sup>.

From the present calculations it was found that the number of atoms/cm<sup>3</sup> (N) is in general of the order of 10<sup>22</sup> atoms/cm<sup>3</sup>. The silver containing glasses had N greater than in vanadate glasses and the bismuth containing had N lesser than or of the order of the N in vanadate glasses.

The radius of the polaron seems to decrease with the addition of the silver/bismuth particles.

To find the effect of the silver and/or bismuth particles on activation energies, it is necessary to calculate the variation of the same as a function of the site separation (R).

It is assumed that the Killias<sup>(41)</sup> model of random jump distance holds. At the instant of hopping,

polarization clouds are created at the two sites, and these overlaps giving a partial reduction in  $W_H$ . Killias<sup>(41)</sup> proved formally that  $W_H$  increases linearly with site separation, thus

$$W_H = W(R_0) + \bar{a}(\Delta R) \quad (38)$$

The fluctuations in  $R (= \Delta R)$  generates a random potential ( $\bar{a} \Delta R$ ). From eqns. (43) and (3), we get

$$\bar{a} = \frac{dW}{dR} \approx \frac{W_H}{2R_0} \quad (39)$$

This can be combined with the tunnel term in eqn. (18). Thus the fall off with distance ( $\alpha$ ) is increased to,

$$\alpha + \bar{a}/2kT \quad (40)$$

This term ( $\bar{a}/2kT$ ) has been calculated both at 500°K and 100°K for different glasses and is tabulated in Table 5. We observe that in silver containing glasses  $(\bar{a}/2kT)_{100^\circ K}$  increases with the silver concentration and in bismuth containing glasses  $(\bar{a}/2kT)_{100^\circ K}$  is usually greater than  $(\bar{a}/2kT)_{500^\circ K}$ .

To detect the variation of conductivity with the addition of silver/bismuth the  $\log \rho$  versus  $1/T$  of all the seven glasses were plotted together (figure 8).

Since it has been found<sup>(6)</sup> that the conductivity varies with the variation of the ratio  $V^{4+}/V_{\text{tot}}$  and also with the mole percent of  $V_2O_5$  in the glass, the observed values of conductivity require normalization with respect to these quantities.

Here it was assumed that the conductivity varies in a Gaussian way around  $V^{4+}/V_{\text{tot}} = 0.11$ , and the reported<sup>(6)</sup> variation for 90 mole percent of  $V_2O_5$  holds. The observed values have been indicated in fig. (8) on the  $V^{4+}/V_{\text{tot}}$  versus conductivity curve.

Normalizing the conductivity values to 1.0 from this curve a graph of conductivity with mole percent of  $V_2O_5$  has been plotted in fig. 8.

This shows that with the addition of silver/bismuth the total conductivity at 25°C is reduced by approximately on order of magnitude and the difference increases with lowering of  $V_2O_5$  mole percent in the case of bismuth and decreases in the case of silver.

To find the temperature ( $T_F$ ) at which the single phonon freeze out starts, a plot of activation energy variation with temperature has been drawn in fig. 9. It seems that the temperature ( $T_F$ ) increases with the addition of bismuth/silver. A hump in the curve was found around 110°K, for the 5 mole percent silver containing glass.

#### 4.2 Surface Conductivity Measurements:

The vanadate glasses and the silver/bismuth containing glasses were reduced in hydrogen atmosphere for 4 hours and their surface conductivities were measured with gold electrode (Table 6, figure 26). Except for the decrease in the conductivity no appreciable change was found between the vanadate glasses and the silver/bismuth containing glasses.

The activation energies calculated were approximately half the same from bulk conductivity measurements.

#### 4.3 A.C. Conductivity:

A variation of A.C. resistivity with temperature has been plotted for a temperature range of 300°K to 100°K, and a frequency range of 100 KHz to 20 Hz for the glasses 1, 3, 4 and 7, in the  $\log$  versus  $10^3/T$  curves (figures 10 to 13). They show a linear increase at higher temperatures, which becomes independent of temperature at lower temperatures. At higher frequencies the flattening is faster. This observation is similar to the behaviour reported for vanadate glasses by the earlier workers<sup>(3,6)</sup>.

To find the variation of conductivity with frequency a plot of  $\log$  (resistivity) versus frequency is

made in (fig. 14). The values of the slope ( $m$ ) have been tabulated in Table 7. It was found that at lowest temperatures the slopes tend to a value 1.0 and at higher temperatures it tends to zero. No natural tendency for a change in  $m$  has been found with the addition of bismuth/silver. However in glass 4 with 10 mole percent of silver a value of  $m = 2$  has been found at very low temperatures. Otherwise all the glasses have values less than one. At lower frequencies these curves deviate from linearity which depends on the relaxation process of the material as suggested by eqn. (26).

#### 4.4 Dielectric Constant Measurements:

The real and imaginary parts of the dielectric constants were calculated as described in Section 3.7.2. The  $\epsilon'$  values have been plotted for the glass no. 1 in the  $\epsilon'$  versus temperature curve (fig. 15). It is compared with the curve reported by Sayer and Mansingh<sup>(6)</sup>. They show an overwhelming similarity, except for at low temperatures, the high frequency values increase. This is thought to be due to some differences in the a.c. conductivity measured. The lower frequency curves have a sharper peak, which broaden at higher frequencies. The peaks for higher



frequencies occur at higher temperatures. These facts are similar to that observed by Sayer and Mansingh. These facts prove the reliability of the present measurements.

The  $\epsilon'$  and  $\epsilon''$  have also been plotted (figs. 16, 17) as a variation with frequency. The dispersion of  $\epsilon'$  is of the order of 1-5, which is found to decrease with decreasing temperature.

The frequency (max) has been plotted as a function of temperature (fig. 16). This gives an activation energy of  $\phi = 0.158$  ev. [using the relation  $\tau = \tau_0 \exp(-\phi/kT)$ ].

The variation of  $\epsilon'$  and  $\epsilon''$  with frequency for the glasses 3, 4 and 7 have been plotted in the figures 18 to 22. It has been observed that the value  $\Delta\epsilon' = \epsilon'_0 - \epsilon_\infty$  increases with the addition of silver or bismuth, drastically.

Using equation (25) an estimation of the disorder activation energy was made in the glasses 1, 3 and 7. They have been tabulated in Table 8.

It is known that  $\frac{1}{2} W_P = W_H = e^2/4 \epsilon_\infty r_P$ ; where  $r_P = \frac{1}{2} (\pi/6)^{1/3} a$ . From this equation the constant  $W_H$  were found and hence the  $r_P$  - the polaron radius was calculated (Table 9). Austin and Mott<sup>(39)</sup> found that  $W\epsilon_\infty$  remains a constant in vanadate glasses.

Using the relation  $W_H = A \epsilon_\infty$  suggested by Nester and Kingery<sup>(42)</sup>. The constant  $A$  for vanadate glasses and for the glasses containing silver/bismuth were calculated. An estimation of  $\epsilon_\infty$  was done from the values of  $A$ , for the glasses 2, 5 and 6 also.

The radius of the polaron calculated seems to decrease with the addition of silver/bismuth. This tallies with our calculation from d.c. conductivity.

#### 4.5 Optical Properties:

The absorption coefficient ( $\alpha$ ) was calculated as described in Section 3.9. The plots of  $(h\nu\alpha)^{1/2}$  versus energy is given in figure (25), for the vanadate glasses containing silver/bismuth. A similar measurement for the glass 1 could not be made because of difficulties in blowing a thin film. So the results are compared with the glass 1 curves reported earlier by Austin<sup>(3)</sup>. A peak was observed at 3.5 ev for glass 4, 3.6 ev for glass 3 and 4 ev for glass 5.

Klinger<sup>(43,44)</sup>, Reik and Heese<sup>(45)</sup> have shown that

$$\sigma(\omega) = \sigma(0) \exp(-\omega \tau_h^2) \frac{\sinh(\hbar\omega/2kT)}{\hbar\omega/2kT} \quad (47)$$

where  $\tau_h^2 = \hbar^2 / W_H kT$ .

This predicts a peak at  $\hbar\omega = 4W_H$ .

In glasses with the same composition as glass 1 peaks have been observed at 1.8 ev which is approximately 4 times 0.319 ev the observed  $W_H$  at high temperatures. However in glasses with silver/bismuth the peak observed was at much higher values compared to  $4W_H$  (Table 10).

#### 4.6 Switching Properties:

Switching was studied in vanadate glasses containing silver/bismuth, both in the bulk form as well as in the thin film form. Switching was not observed in the glass 1 and 2 even at very high temperatures (250°C). It was also not observed on hydrogen reduced surfaces of these glasses.

Glass 3 and 4 were studied for switching. The glass 4 had memory switching characteristics as given in figure 27. However these switching properties were destroyed due to thermal cycling (also see Table 11 for OFF and ON state resistances). The switching voltage increased with increasing temperature exponentially as shown in figure 33.

Glass 7 was studied in the bulk form and the typical curves are shown in figure 28. They had memory type switching properties at higher temperatures and had threshold type switching properties at lower temperatures. The switching was not destroyed due to thermal cycling and the characteristics remained similar. At room temperature after the thermal cycling a memory switching was observed from  $\rho = 6.7 \times 10^4 \Omega \text{ cm}$  to  $6.0 \times 10^3 \Omega \text{ cm}$ . With this ON state as the primary state, another switching of the threshold type was observed to  $3.0 \times 10^3 \Omega \text{ cm}$  (fig. 28.2). This threshold switching was observed for millions of times, using the pulse method, on an oscilloscope. The switching was found stable and did not decay with time (observation was done for 2 days). The observation at different applied voltages have been recorded in fig. 29.

The threshold voltage for the memory switchings have been drawn as a function of temperature. It seems to increase with temperature similar to that in glass 4.

Glass 5 was studied in the thin film form. Memory switching was observed after the first thermal cycling was done. Stable memory switchings were observed at higher temperatures. This memory type switching slowly turns to the threshold type of switching below  $70^\circ\text{C}$ . The periodical curves are given in fig. 30. At

room temperature ( $30^{\circ}\text{C}$ ), it shows a clear threshold switching which has a stable negative resistance region. Negative resistance observed was ( $- 38 \Omega$ ). This character was repeated again for millions of times by using pulse method (figures 31 and 32). Just to make sure this was not accidental, the measurements were repeated for an another glass of the same composition and of a higher thickness. Except for a change in switching voltage which occurs due to the thickness, the character of switching was found very much reproducible. The threshold voltage was drawn as a function of temperature (fig. 33) both for the threshold and memory type of switching..

For the threshold switching the temperature decreases with increasing temperature. But for the memory type, the  $V_{th}$  increases with temperature, as found in glass 4 and 7 (bulk). The  $V_{th}$  becomes zero at  $68^{\circ}\text{C}$  for the threshold type of switching in glass 5.

Glass 6 was also studied in the thin film form. The figure 33 gives the  $V_{th}$  as a function of temperature which show an increase with temperature.

Both in glass 5 and 6 the ON state resistances ranged from 10 to 50 ohms.

## CHAPTER 5

## DISCUSSION

## 5.1 Electrical Conductivity:

The total activation energy drops to the disorder activation energy in all the glasses.

Glass 3 shows a two step freezing. The activation energy versus temperature curve shows a hump at 110°K (this effect occurs only at low temperatures because it is the part affected more by the disorder). This could be explained by the following model.

Although it has been assumed hitherto that the silver precipitates as silver particles, there is a finite possibility that it may go into the matrix as ions. This is supported by the number of atoms/cm<sup>3</sup> which rises only in the case of glass 3, and also the radius of the polaron ( $r_p = 4.15 \text{ \AA}$ ) which is greater than in glass 1 ( $r_p = 1.732 \text{ \AA}$ ). The first freezing in glass 3 could be due to the freezing out of the electron hopping between silver ions and vanadium ions. The second freezing could be due to freezing of electron hopping assisted by optical phonon between the different valent vanadium ions. The number of atoms/cm<sup>3</sup> participating in the hopping after

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the first freezing ( $N = 87 \times 10^{22}$  atoms/cm<sup>3</sup>) is greater than after the second freezing ( $N = 37.1 \times 10^{22}$  atoms/cm<sup>3</sup>). This shows that the silver ions participation ceases at lower temperatures, i.e. electrons would not accept silver as a site for hopping at lower temperatures.

The total conductivity observed is due to a mixed effect arising from the hopping of electron between the different valent vanadium sites and silver. However this model needs confirmation from more experiments on silver containing glasses as well as the electron microscopic studies.

There are different possibilities of the same not occurring in the glass 4 with a higher percentage of silver. They are:

- (1) Glass 4 contains lesser percentage of  $V_2O_5$ , so it is possible that the interaction between the vanadium ions and the silver ions are submerged in the total conductivity.
- (2) The two processes may freeze out simultaneously.
- (3) The silver ions may not be present.

To identify the same ~~more~~ data is necessary on similar glasses. Glasses containing bismuth also do not show any such double freezing effects.

It has been observed that the random potential  $(\bar{a} \Delta R)$  at lower temperatures ( $100^\circ\text{K}$ ), generated due to the fluctuations in  $R$  - the site spacing, increases with the increase in silver content. So the effects due to silver must be predominant in the case of glass 4.

In the case of bismuth containing glasses  $(\bar{a} \Delta R)_{100^\circ\text{K}}$  is greater than  $(\bar{a} \Delta R)_{500^\circ\text{K}}$ . This is possibly why the  $(W_H)_{100^\circ\text{K}}$  calculated from  $C$  is greater in bismuth containing glasses than the others.

## 5.2 A.C. Conductivity:

For the frequency dependence of a.c. conductivity a hopping process model has been proposed by Jonscher<sup>(46)</sup> which gives

$$\sigma(\omega) = A \omega^2 \sum_{m=1}^N t_m \quad (48)$$

where,  $t_m$  is the number of hops. This model for an infinite sequences of events gives a  $\sigma(\omega) \propto \omega^m$  where  $m$  has a value between 0 and 1 depending upon the temperature. It has been seen that<sup>(46)</sup>, no values of exponent ' $m$ ' greater than unity can be generated by physically plausible sequences of events  $t_m$ , with the exception of  $m = 2$ .



It has also been shown by experimental evidence that  $m$  greater than 1 is not possible. The value of 2 for  $m$  can arise due to any sequence of a finite number of hopping events terminating at a time  $t_{lim}$ .

A finite chain of identical steps with one electron on it gives a limited rise to a limited sequence of hops which ceases when the carrier has reached the end of the chain. We would therefore expect a  $\omega^2$  dependence as was found theoretically by a different argument by Beeby and Hayes<sup>(47)</sup>. Experimentally such a hopping has been found in polymeric  $CS_2$  by Chan and Jonscher<sup>(48)</sup>.

Looking at the present results all the glasses except glass 4 have shown the frequency dependence with  $m$  less than 1. This is also in accordance with the eqn. (26). At lower frequencies the curve deviates from linearity depending on the relaxation process.

In glass 4, however, at the temperature 116°K, at high frequencies a dependence of  $m = 2$  has been found. At higher temperatures  $m$  less than 1 dependence is shown. This can be explained from the above discussion that a finite number of hops exist.

This can occur because of the high concentration of silver as was expected from the calculations of  $\bar{a}/2kT$  (Section 5.1). Now let us assume that there are chains of

silver particles in the  $V_2O_5 - P_2O_5$  matrix. We have shown from the d.c. conductivity that there exists a mixed hopping. At lower temperatures (as low as  $100^\circ K$ ) the  $V^{4+} - V^{5+}$  hopping would cease. But still the electron can easily move in the chains of silver particles. Probably this is what that arises the  $m = 2$  a.c. conductivity dependence, at higher frequencies and lower temperatures. This proves the already made assumption that silver particles actively participate in the hopping process.

### 5.3 Dielectric Constant Measurements:

The glass 1 shows peaks in  $\epsilon''$  which move to higher temperatures as the frequency increases. They have values ranging from 1-10.

Glass 3 shows  $\epsilon'$  and  $\epsilon''$  values higher than in glass 1. The  $\epsilon''$  variation does not show any peaks.  $\epsilon'$  values range from 1-50.

Glass 4 has still higher values ( $10^3 - 10^4$ ) of  $\epsilon'$ . Glass 7 has also shown very high values of  $\epsilon'$  and  $\epsilon''$ .

To confirm that they were not due to any contact polarization effects the capacitance values were plotted as a function of frequency. Except glass 4 which shows a comparatively large dispersion at high temperatures, the gold contact on all the glasses does not show any space charge polarization (fig. 24). So the cause for such

high values of  $\epsilon'$  and  $\epsilon''$  were thought to be due to the silver/bismuth particles embedded in the glass matrix which give a Maxwell-Wagner polarization. However a quantitative calculations cannot be done here since the size of the particles and their existence are not known. For such an analysis the electron micrographs of the glasses are necessary.

The peaks in the  $\epsilon''$  can be calculated from the  $\epsilon'$  values obtained from the Kramers-Kronig relations as described by Lowell<sup>(49)</sup>.

#### 5.4 Optical Properties:

They show peaks at energies greater than  $4W_H$  contrary to that expected in vanadate glasses. In deriving the expression  $\hbar\omega = 2W_P = 4W_H$  an assumption has been made<sup>(39)</sup> that the overlap integral ( $J$ ) is small. But without assuming the same, we get

$$\hbar\omega = 2W_P = 4W_H + 2J$$

Our observation shows that the overlap integral seems to increase with the addition of silver/bismuth. This is in accordance with the tunnel term ( $\bar{a}/2kT$ ) calculations. However an exact calculation is difficult to make at present.

### 5.5 Switching Properties:

The switching observed in all the glasses were due to the existence of silver/bismuth particles, since they were not observed in the base glasses 1 and 2. No memory switching has been reported in the vanadate glasses hitherto, this also goes to prove the switching are due to the existence of silver/bismuth particles.

In all the cases the threshold voltage of the memory switching increases with temperature. The memory switching could be due to two possibilities,

- (1) Formation of crystalline material in between the particles.
- (2) Formation of filaments with a chain of silver/bismuth particles.

The second possibility seems to be more adequate since such a chain formation was detected in the a.c. conductivity measurements in glass 4.

The increase in threshold voltage for memory switching with temperature is probably because with increasing temperature disorder in the material increases and a chain formation becomes more difficult and hence a higher voltage is necessary for the formation of filaments.

In glass 7 and 5 threshold switching was observed at lower temperatures. The threshold voltage for

~~the~~ threshold switching in glass 5 shows a decrease with increasing temperatures and cuts off at 68°C. This is exactly similar to the observation made in vanadate glasses by Reagan and Drake<sup>(50)</sup>. They have shown that with a proper selection of  $V^{4+}/V^{5+}$  ratio (range of 10-27%) threshold voltage switching can be observed. The threshold/in their case also decreases with increasing temperature cutting off at 68°C. They also found that the thermal expansion has a discontinuity in the thermal expansion versus temperature curve at 68°C. From this it was suggested that some interaction between  $VO_6$  octahedra takes place at 68°C. They did not observe any change in the character of switching with the addition of different oxides of metal.

The above observation by Reagan and Drake suggests that the threshold switching in glass 5 was due to the base glass and has nothing to do with the bismuth particles. The threshold switching was observed in glass 5 and not in glass 1 and 2, possibly because the addition of  $Bi_2O_3$  has changed the oxygen state so as to lie within the range in which one can expect a threshold switching.

The memory switching found in these glasses and the change in the threshold voltages as a function of temperature in contrary to the observation of Reagan that the addition of oxides does not change the character of

switching, suggests that the bismuth do not go as ions in these glasses, but are present as neutral particles.

At room temperature a threshold switching was observed with negative resistance. This arises as a combination of the memory as well as threshold character. This suggests that from a proper combination of the base glass and the percentage of bismuth added one could produce a glass having the required character of switching.

In the silver containing glasses (glass 4) the switching was not stable and were also destroyed in thermal cycling. Hence they are not thought as a prospective material for switching purposes. This is probably because the silver has relatively high melting point and hence it is difficult to form filament out of these particles under the present experimental conditions.

The resistances in ON state was less than 50 ohms in most of the cases when measurements were done on thin films. In the case of bulk glasses it ranged from  $10^2$  to  $10^3$  ohms. This is possibly because, in bulk glasses the filaments and the matrix behave as a composite and the effective resistance is observed, and in the thin films possibilities of single filaments between the electrodes exist.

Although various experimental evidences show that bismuth is present as neutral particles in the glass matrix, this needs confirmation by electron microscopic investigation.

The present studies also show that the material, vanadate glasses incorporated with bismuth particles can be exploited as a switching material for suitable commercial applications.

## CHAPTER 6

## CONCLUSIONS

The following conclusions were drawn from the present investigations:

- (a) The d.c. conductivity measurements show a lowering of conductivity with the addition of silver/bismuth, contrary to the earlier observation with metal oxide additions.
- (b) The long range tunnelling of electrons increases with the addition of silver/bismuth.
- (c) The glass with the composition ( $75\text{P}_2\text{O}_5$ ,  $15\text{P}_2\text{O}_5$ ,  $10\text{Ag}$ ) shows in the a.c. conductivity variation with frequency measurements a possibility of silver particles linking up to form chains at lowest temperatures.
- (d) The high temperature activation energies calculated from dielectric measurements agree reasonably with those estimated from d.c. conductivity measurements.
- (e) The polaron radius ( $r_p$ ) calculated both from the d.c. and a.c. conductivities show a decreasing tendency with addition of silver/bismuth.



- (f) Optical absorption studies also indicate an increase in the overlap integral (J) with the addition of silver/bismuth.
- (g) Switching studies indicate strong possibilities of getting reproducible switching devices with the addition of bismuth.
- (h) The switching mode depends on the temperature of operation.
- (i) A negative resistance device, purely threshold switching device, threshold switching with negative resistance and memory switches could be produced with a proper combination of the  $V^{4+}/V_{tot}$  ratio in the base glass and the mole percent of bismuth added, keeping in mind the temperature of operation. The change in resistance between the ON state and the OFF state can be controlled by the thickness of the material.

Table 1

The chemical compositions of the glasses chosen for the present investigation

Glass No.	Composition of (in mole percents)			
	$V_2O_5$	$P_2O_5$	Ag	Bi
1	80	20	-	-
2	70	30	-	-
3	80	15	5	-
4	75	15	10	-
5	80	15	-	5
6	75	15	-	10
7	70	15	-	15

Table 2

The stable compounds belonging to the V-O system

Oxide	Crystalline structure	Theoretical density $g/cm^3$	Melting point $T^\circ C$
VO	Cubic	5.23	2050
$V_2O_3$	Hexagonal	4.87	1970-2000
$VO_2$	Tetragonal	4.65	1545-1640
$V_2O_5$	Orthorhombic	-	609

Table 3

The data from chemical analysis and density measurements

Glass no.	From chemical analysis (in wt%)				Density gm/cm <sup>3</sup>	Site spacing R <sub>O</sub> Å
	V <sup>4+</sup> concn wt%	V <sup>5+</sup> concn	V <sub>2</sub> O <sub>5</sub> concn	V <sup>4+</sup> /V <sup>5+</sup> = v		
1	7.32	40.1	80.3	0.183	2.4925	4.48
2	1.43	40.2	71.6	0.0355	2.45	4.46
3	3.87	45.4	81.2	0.0854	2.8	4.072
4	5.42	39.45	70.6	0.1373	3.52	3.52
5	3.1	39.0	79.6	0.0794	2.87	2.87
6	5.95	35.45	63.4	0.1675	3.525	3.575
7	5.88	29.22	52.1	0.201	3.86	3.86

Table 4

Total activation energy (C in ev) as a function of temperature

T°K	C in ev						
	Glass 1	Glass 2	Glass 3	Glass 4	Glass 5	Glass 6	Glass 7
270	0.319	0.	0.2155	0.296	0.248	0.37	0.338
250	0.319		0.2155			0.2000	0.338
220	0.319		0.2155			0.1835	
200	0.319		0.122	0.296	0.248	0.1835	0.1775
182	0.14		0.0878				
167	0.1165	0.258	0.0482	0.09	0.164	0.1835	0.15
154	0.0992	0.258	0.041				
143	0.0862	0.258	0.0181	0.062	0.1118		
134	0.082	0.258					0.122
125	0.069		0.0495	0.0386	0.0734		
110	0.0346	0.0177	0.0801	0.0364			
100	0.0346	0.0177	0.0557				0.072
91	0.0346	0.0177	0.0257	0.0364	0.0734		0.072

Table 5

Parameters calculated from d.c. conductivity measurements

Glass no.	(Bk) ev	$R_o$ $\text{\AA}$	$W_D$ ev	$N \times 10^{22}$ atoms/cm <sup>3</sup>	$a$ $\text{\AA}$	$r_p$ $\text{\AA}$	$(W_{tot})_{100^\circ K}$ ev	$(\bar{a}/2kT)_{500^\circ K}$ $\text{\AA}^{-1}$	$(\bar{a}/2kT)_{100^\circ K}$ $\text{\AA}^{-1}$
1	0.01448	4.48	0.521	1.135	4.33	1.732	0.0346	0.412	0.224
2	0.002665	4.46	0.01715	3720.0	0.675	2.6	0.0177	0.335	0.115
3a	0.0039	4.072	0.05675	81.5	1.032	4.15	0.0257	0.306	0.183
3b	0.00476		0.123	37.1	1.37	5.55			
4	0.00539	3.52	0.0574	25.8	1.57	0.635	0.0364	0.488	0.3
5	0.00835	2.87	0.608	3.98	2.93	1.18	0.0734	0.502	0.739
6	0.01280	3.575	1.87	0.685	5.38	2.17	0.1835	0.60	1.49
7	0.01045	3.86	0.653	1.57	1.85	0.74	0.072	0.515	0.548

Table 6  
Surface conductivity measurements

Glass no.	No. of hours of H <sub>2</sub> redn	Act. energy (ev)	Act. energy (ev) (Bulk condty.)
1	4	0.2105	0.319
2	4	0.182	0.258
3	4	0.100	0.215
6	4	0.16	0.370
7	4	0.1575	0.338

Table 7

$\mu$  from a.c. conductivity variation with frequency

Glass no.	Temperature, T°K	$\mu$
1	212	0.725
3	130	0.8
3	272	0.00525
4	116	2.0
4	132	0.95
7	142	0.675
7	344	0.125

Table 8

Activation energy from  $1/\Delta\epsilon$  vs.  $10^3/T$  curves

Glass no.	$W_D$ ev	$W_d$ ev (from d.c. conductivity)
1	0.043	0.0173
3	0.0157	0.0129
7	0.0956	0.036

Table 9

Radius of the polaron from dielectric constant measurements

Glass no.	$\epsilon_\infty$	$W_H$ ev	$W_H \epsilon_\infty$	$r_P$ Å
1	4.39	0.319	1.395	2.28
3	11.7	0.2155	2.57	1.56
7	6.384	0.338	2.16	1.855

Table 9 contd.

Table 9:

Approximate calculation of  $\epsilon_\infty$ 

Glass no.	$W_H$ ev	$\Lambda = W_H / \epsilon_\infty$ ev	$(\epsilon_\infty)_{\text{calc.}}$
1	0.319	0.073	4.39 (obs.)
2	0.258	0.073	3.52
3	0.2155	0.0184	11.7 (obs)
4	0.296	0.0184	16.1
5	0.248	0.053	4.68
6	0.370	0.053	6.99
7	0.338	0.053	6.384 (obs)



Table 10  
Optical absorption edge

Glass no.	Absorption peak (ev)	Absorption edge, $E_{opt}$ (ev)
4	-	1.45
4H	3.5	1.55
3	3.6	1.75
5	3.0	1.85
6	-	1.75

Table 11  
Switching data of glass 4 (bulk form)

T°C	$V_{th}$ (memory) in volts	Resistivities (in ohm-cm)	
		OFF state	ON state
48	1.8	$2.225 \times 10^5$	$0.946 \times 10^4$
68	2.8	$1.625 \times 10^5$	$3.5 \times 10^3$
121	3.65	$1.38 \times 10^5$	$2.63 \times 10^3$
138	9.2	$5.00 \times 10^4$	$1.28 \times 10^3$
152	18.0	$2.63 \times 10^4$	$5.0 \times 10^2$
163	24.0	$3.33 \times 10^4$	$4.12 \times 10^2$
185	64.0	$1.925 \times 10^4$	$3.82 \times 10^2$

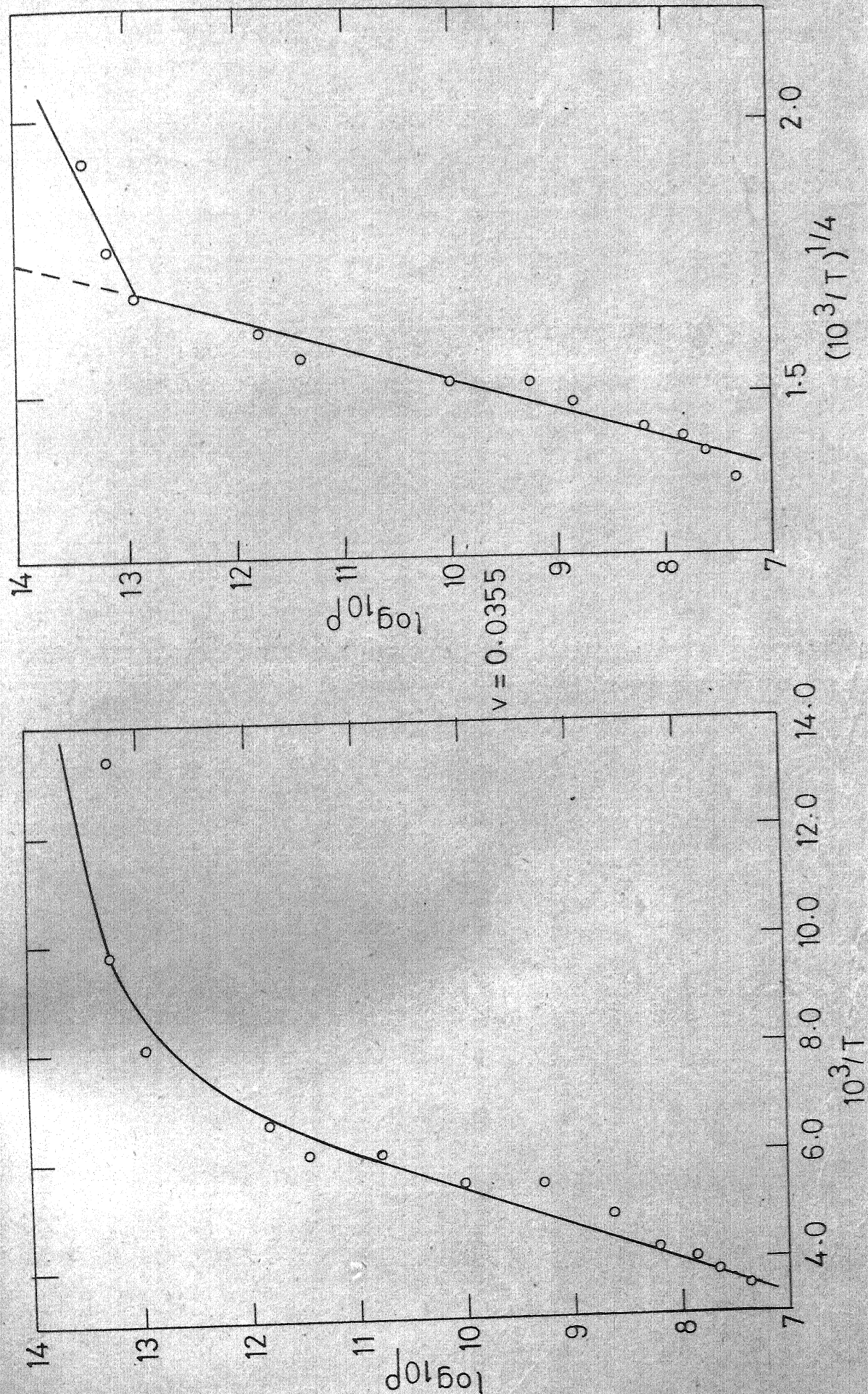


FIG.2 DC CONDUCTIVITY OF GLASS No. 2 70V<sub>2</sub>O<sub>5</sub> 30P<sub>2</sub>O<sub>5</sub>



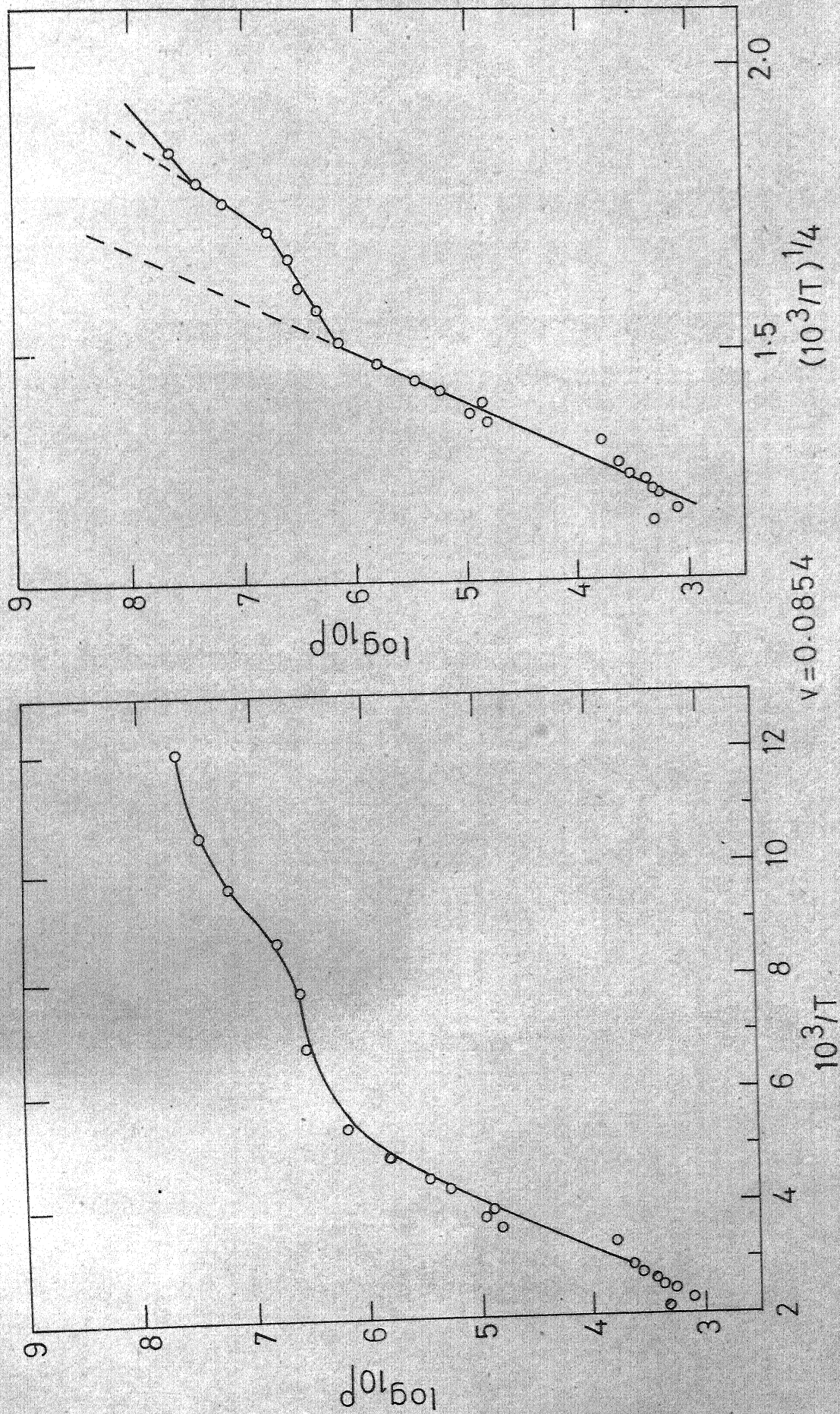


FIG.3 DC CONDUCTIVITY OF GLASS No.3 80V<sub>2</sub>O<sub>5</sub>,15P<sub>2</sub>O<sub>5</sub>,5 Ag



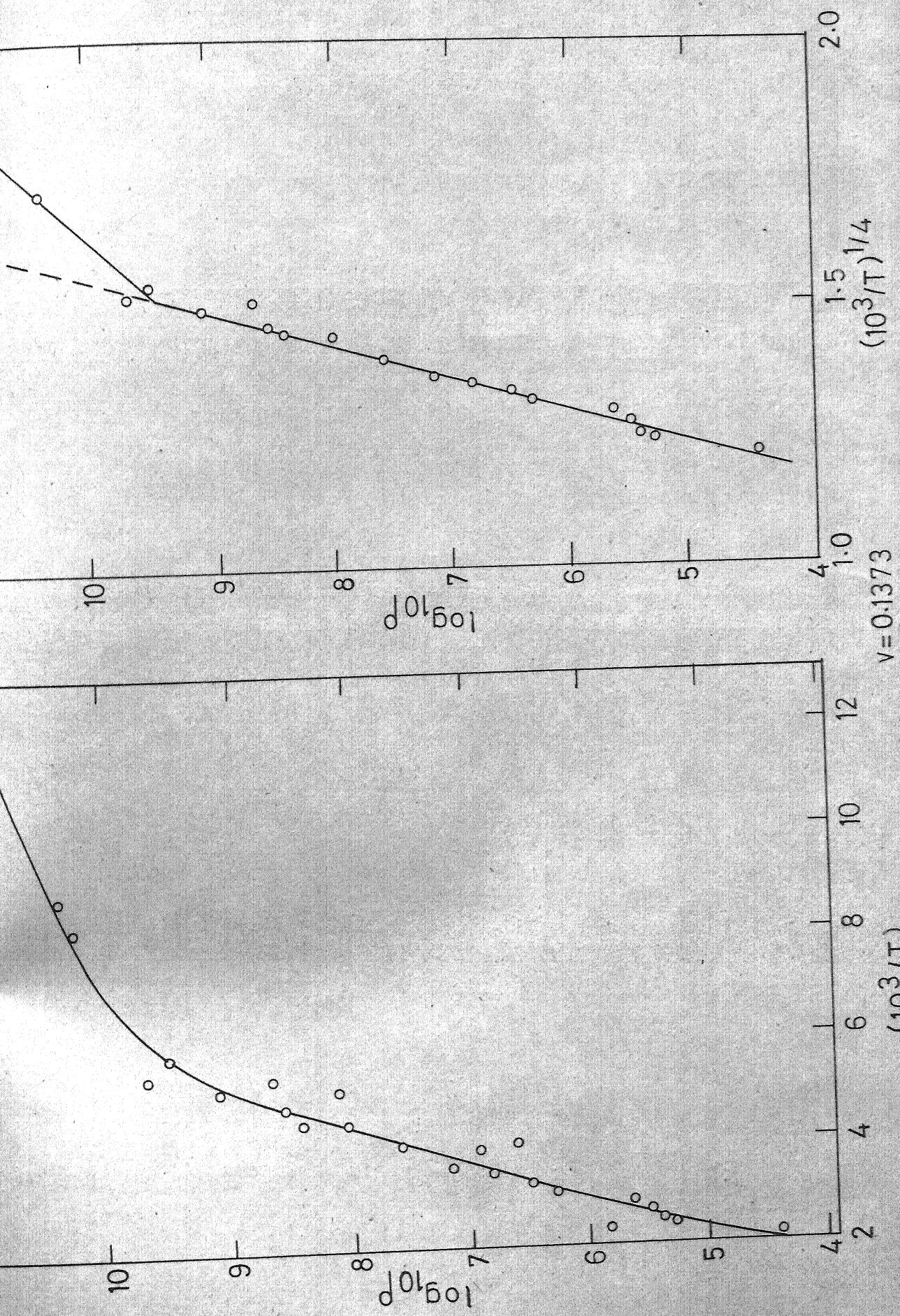


FIG. 4 DC CONDUCTIVITY OF GLASS No. 4 75V<sub>2</sub>O<sub>5</sub>, 15P<sub>2</sub>O<sub>5</sub>, 10Ag



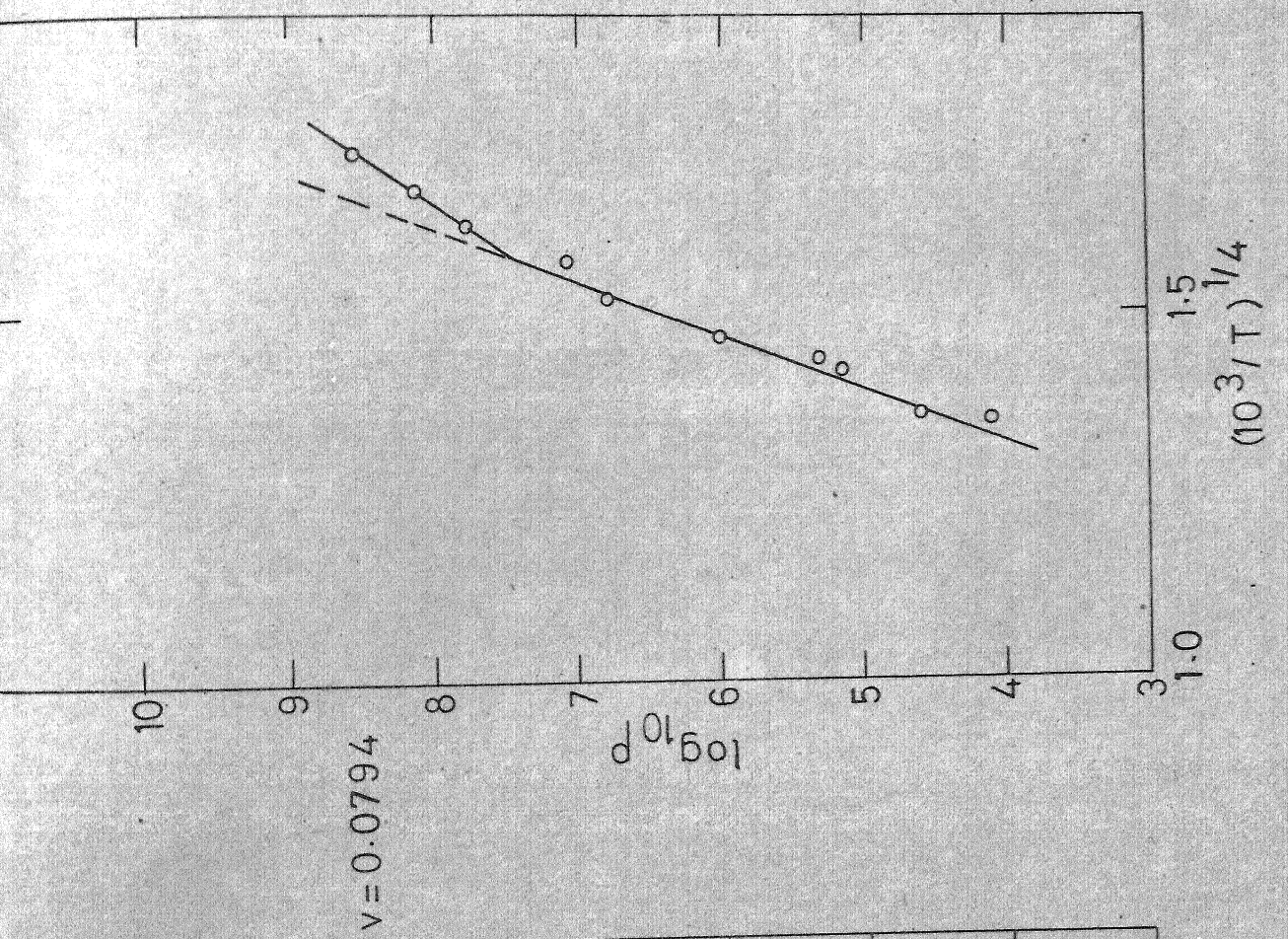
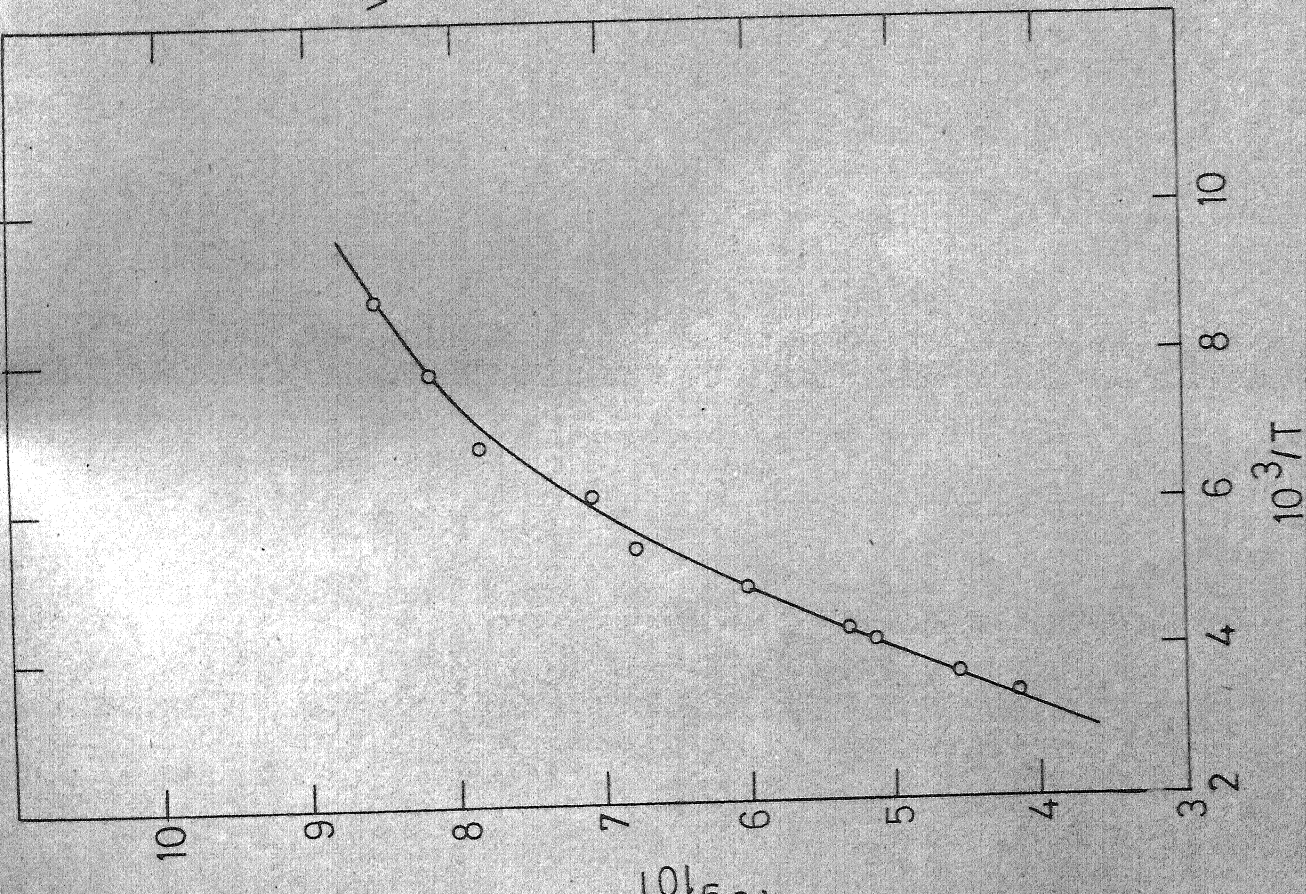


FIG.5.DC CONDUCTIVITY OF GLASS No.5  $80V_2O_5, 15P_2O_5, 5Bi_2O_3$



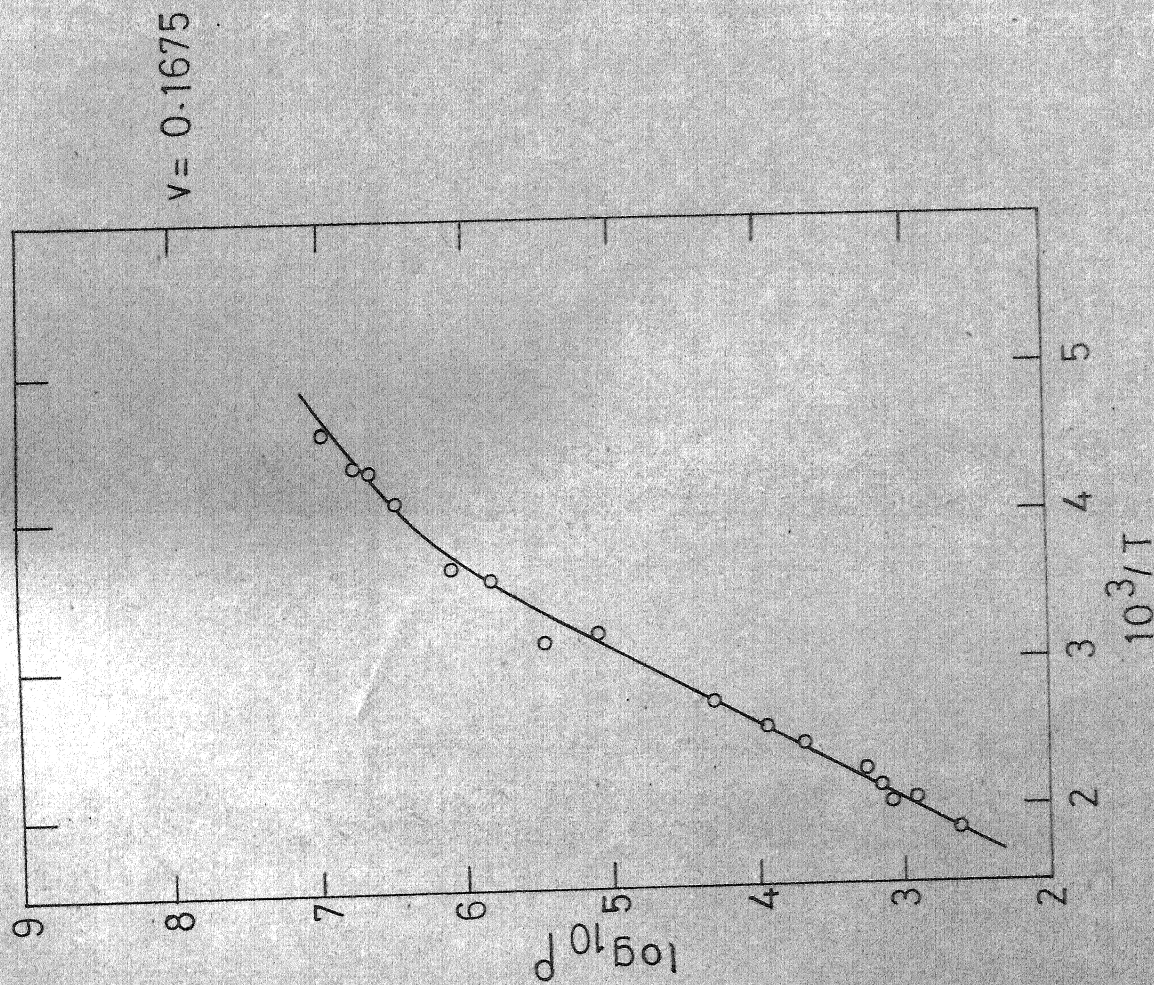
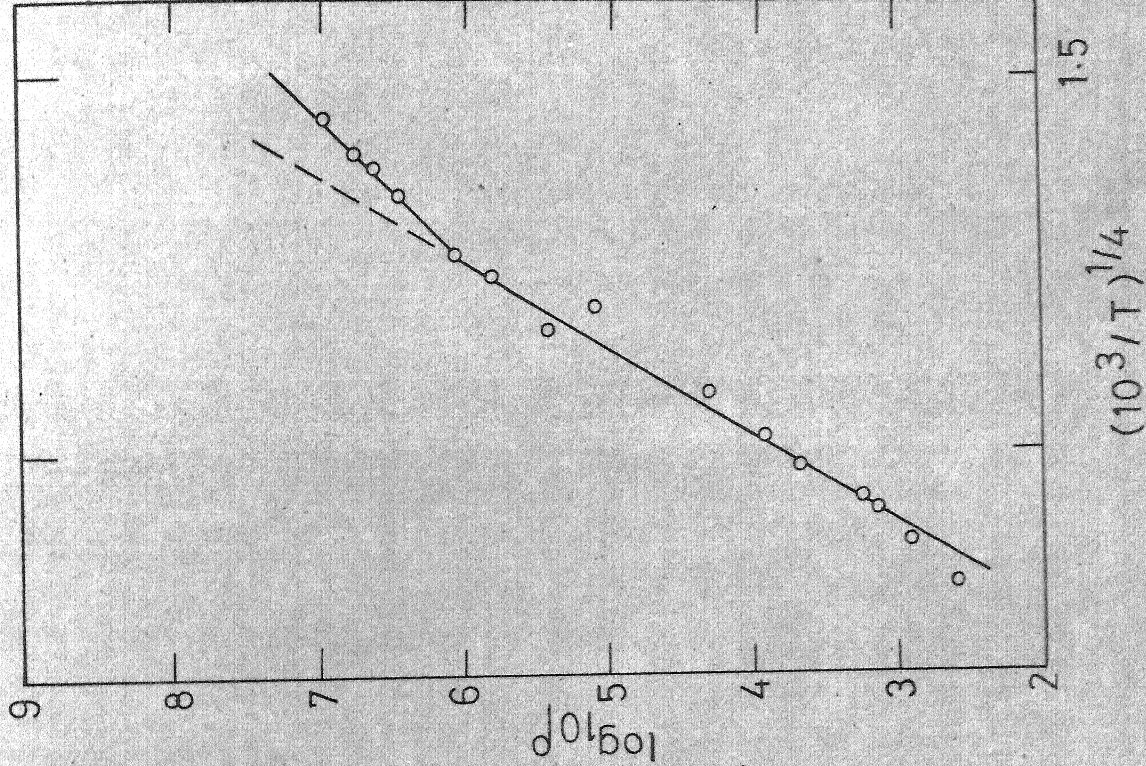


FIG. 6. DC CONDUCTIVITY OF GLASS No. 6 75V<sub>2</sub>O<sub>5</sub>:15P<sub>2</sub>O<sub>5</sub>:10Bi<sub>2</sub>O<sub>3</sub>



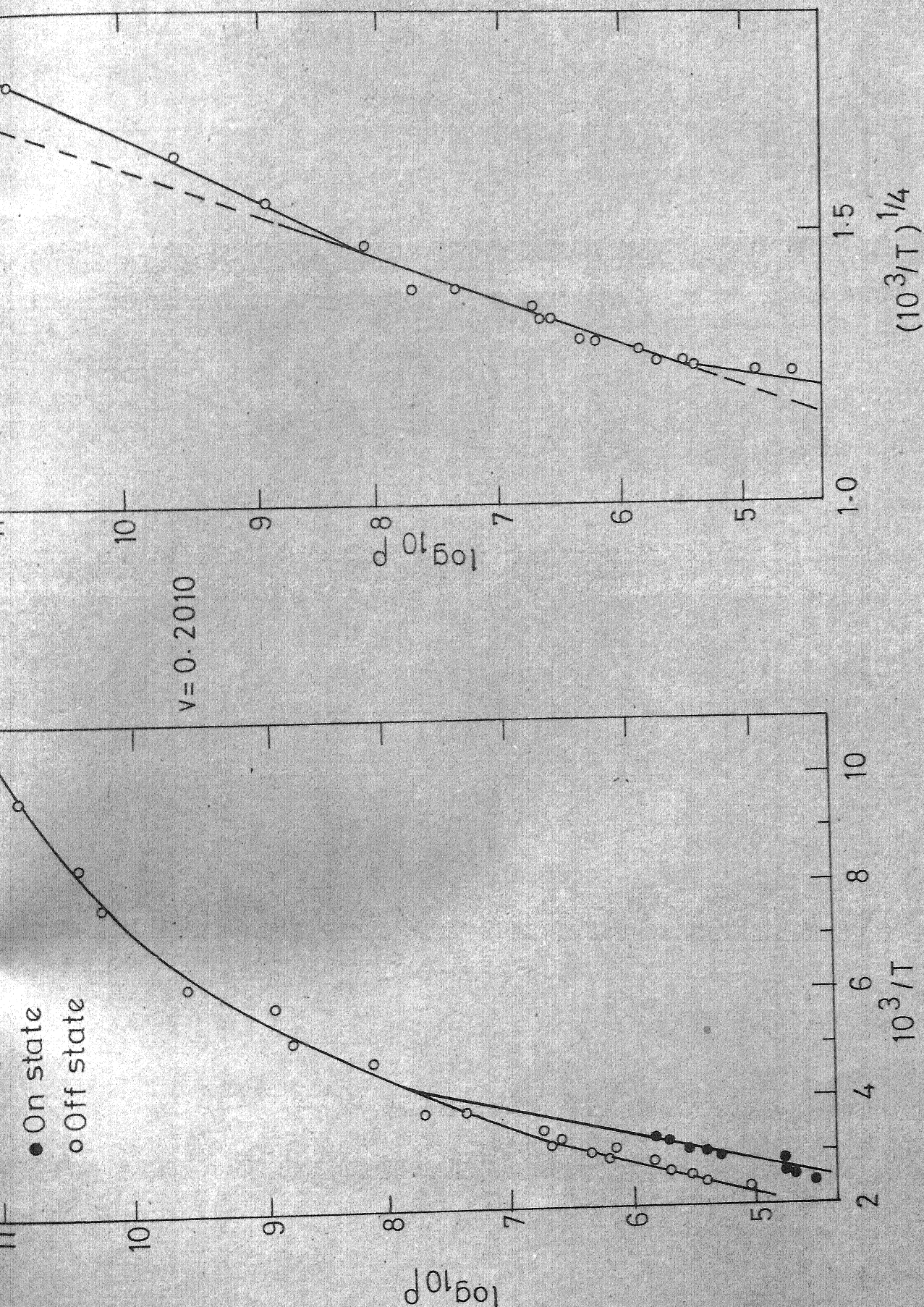
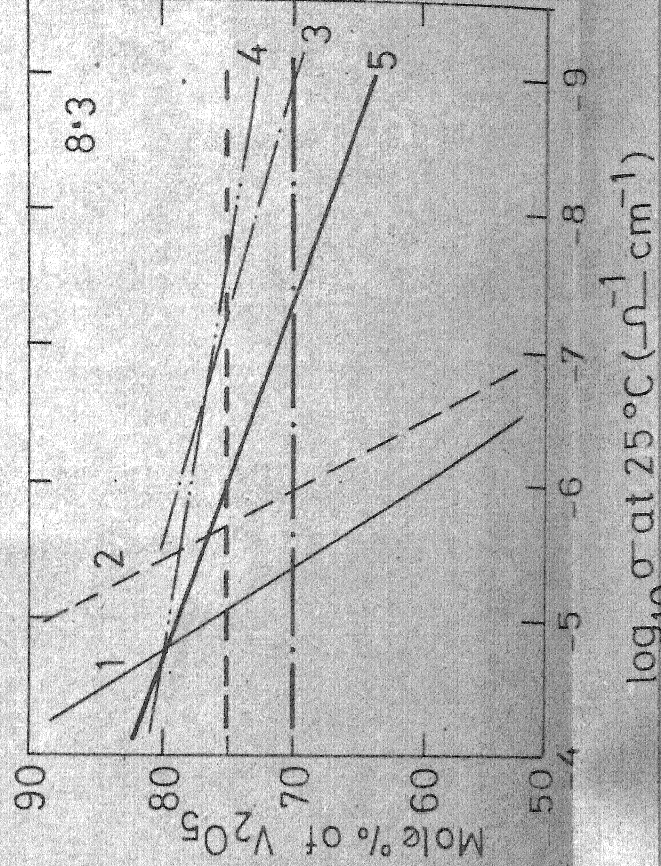
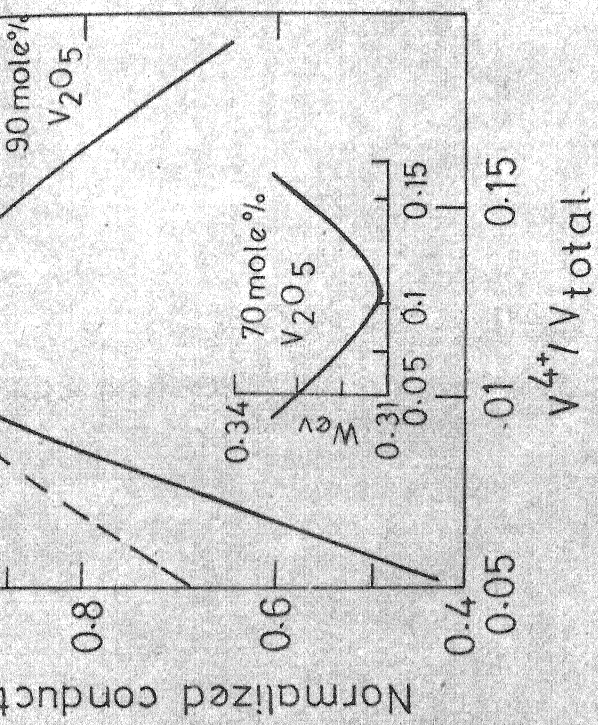
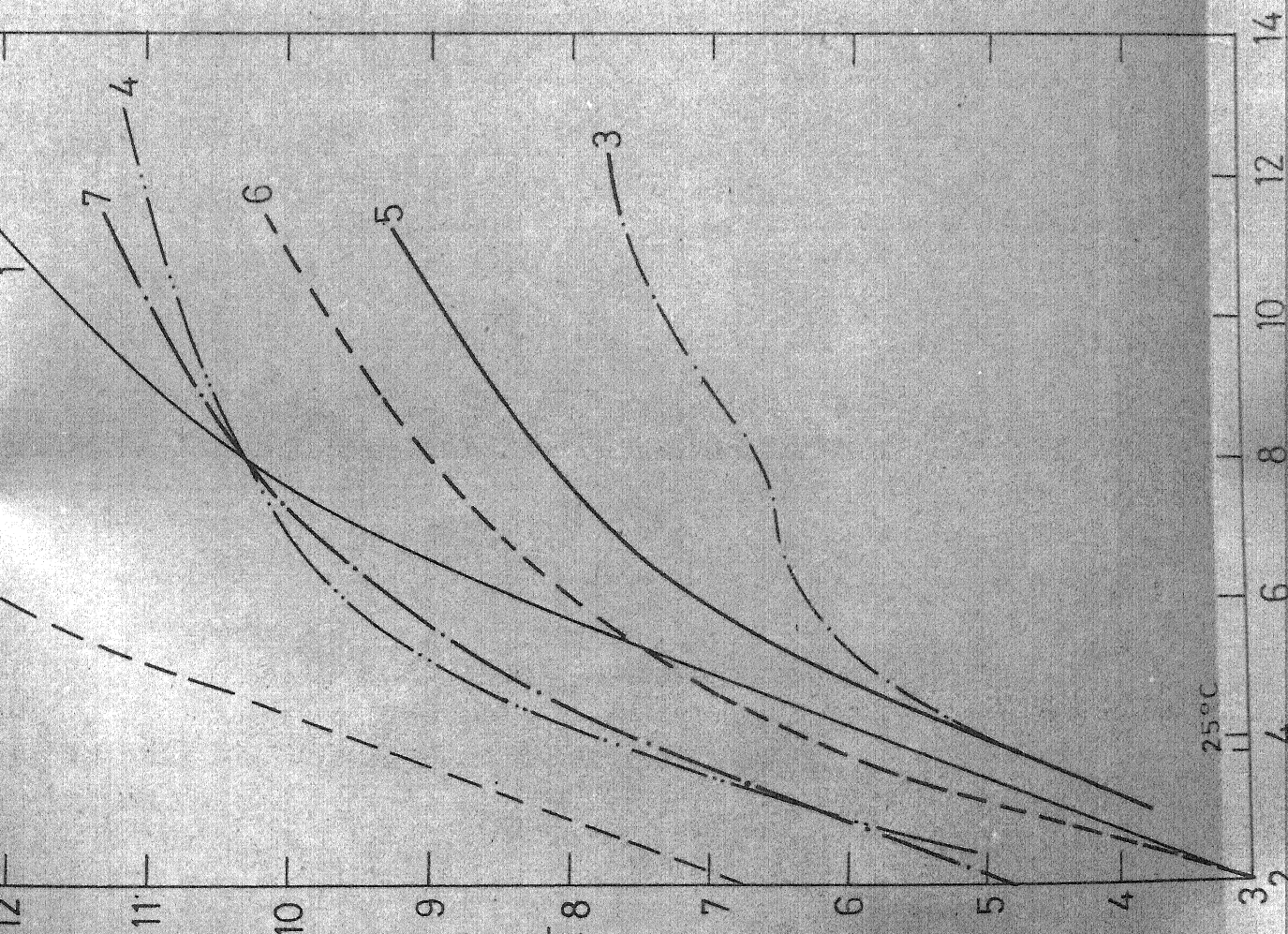


FIG7.DC CONDUCTIVITY OF GLASS No. 7 70V<sub>2</sub>O<sub>5</sub>:15P<sub>2</sub>O<sub>5</sub>:15Bi<sub>2</sub>O<sub>5</sub>







Description of the figure 8

Fig. 8.1:	Serial no.	Glass no.	$v = V^{4+}/V_{\text{tot}}$
	1	1	0.183
	2	2	0.0355
	3	3	0.0854
	4	4	0.1573
	5	5	0.0794
	6	6	0.1675
	7	7	0.2010

Fig. 8.3:	Serial no.	Chemical composition
	1	BaO - $V_2O_5$ - $P_2O_5$
	2	$Na_2O$ - BaO - $V_2O_5$ - $P_2O_5$
	3	$V_2O_5$ - $P_2O_5$
	4	$V_2O_5$ - $P_2O_5$ - Ag
	5	$V_2O_5$ - $P_2O_5$ - $Bi_2O_3$

The curves 1 and 2 are from Sayer and Mansingh's paper<sup>(6)</sup>.  
 The present data is shown in the curves 3, 4 and 5.

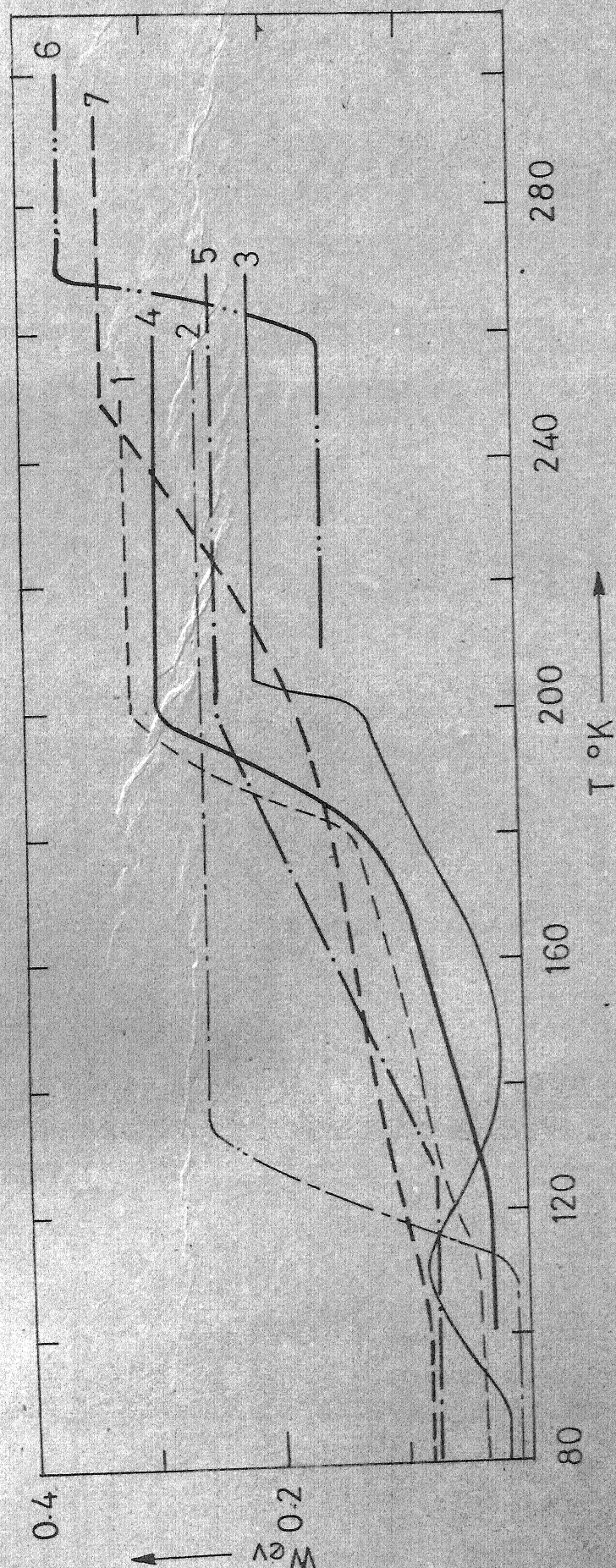


FIG.9 TOTAL ACTIVATION ENERGY VS. TEMPERATURE



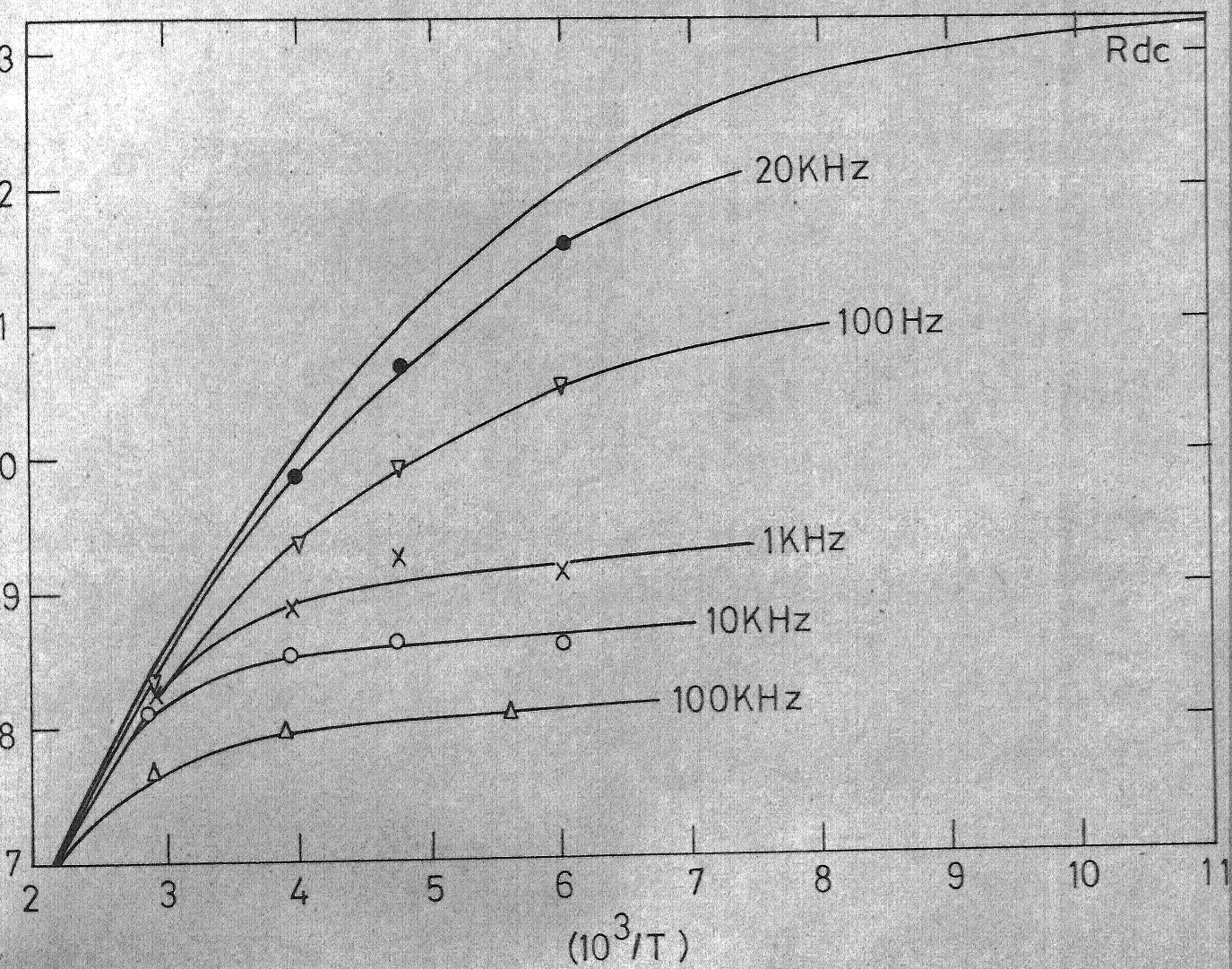


FIG. 10 AC CONDUCTIVITY OF GLASS No. 1 80V<sub>2</sub>O<sub>5</sub>, 20P<sub>2</sub>O<sub>5</sub>



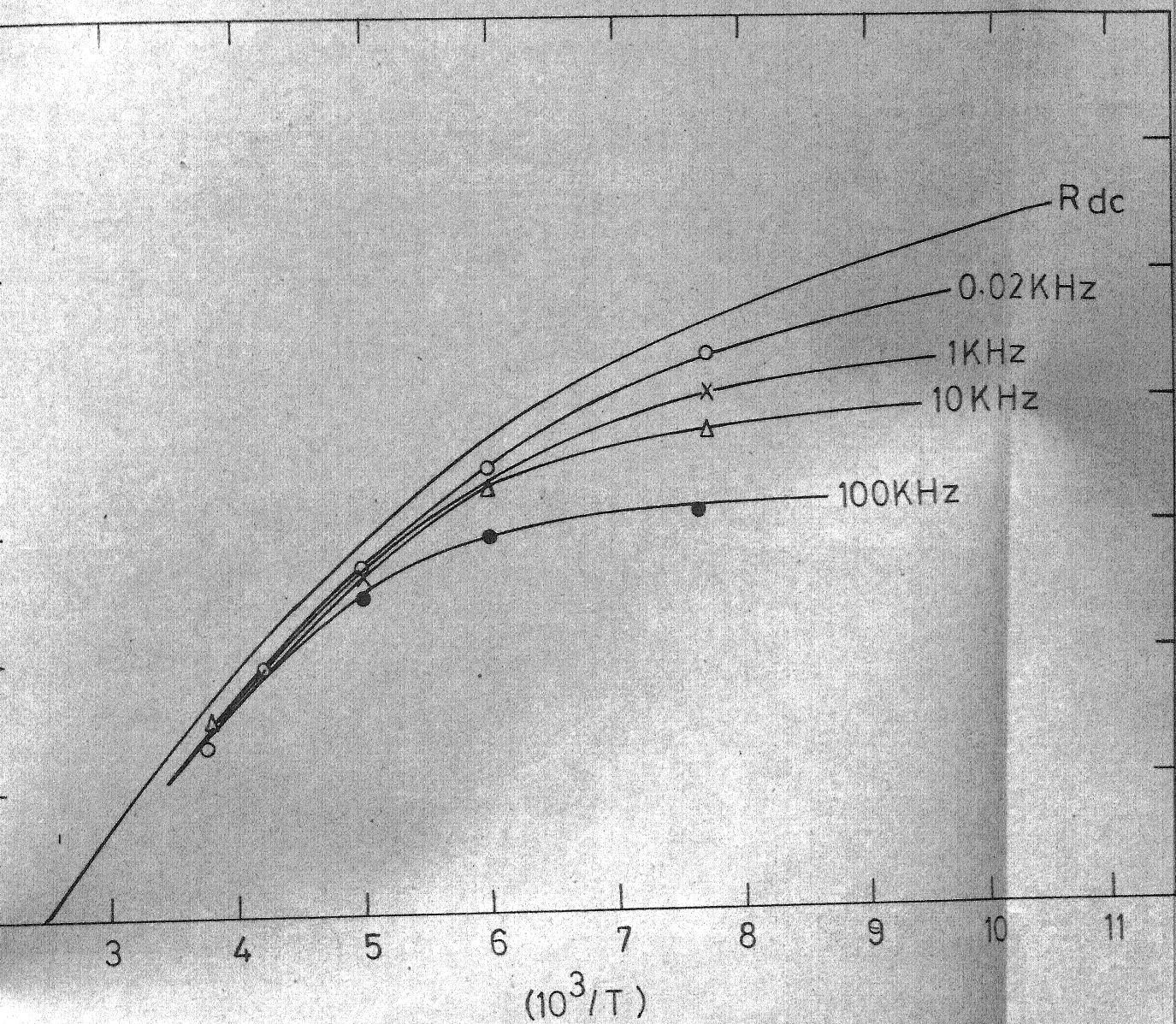


FIG. 11 AC CONDUCTIVITY OF GLASS No. 3  $80V_2O_5, 15P_2O_5, 5P_2O_5$



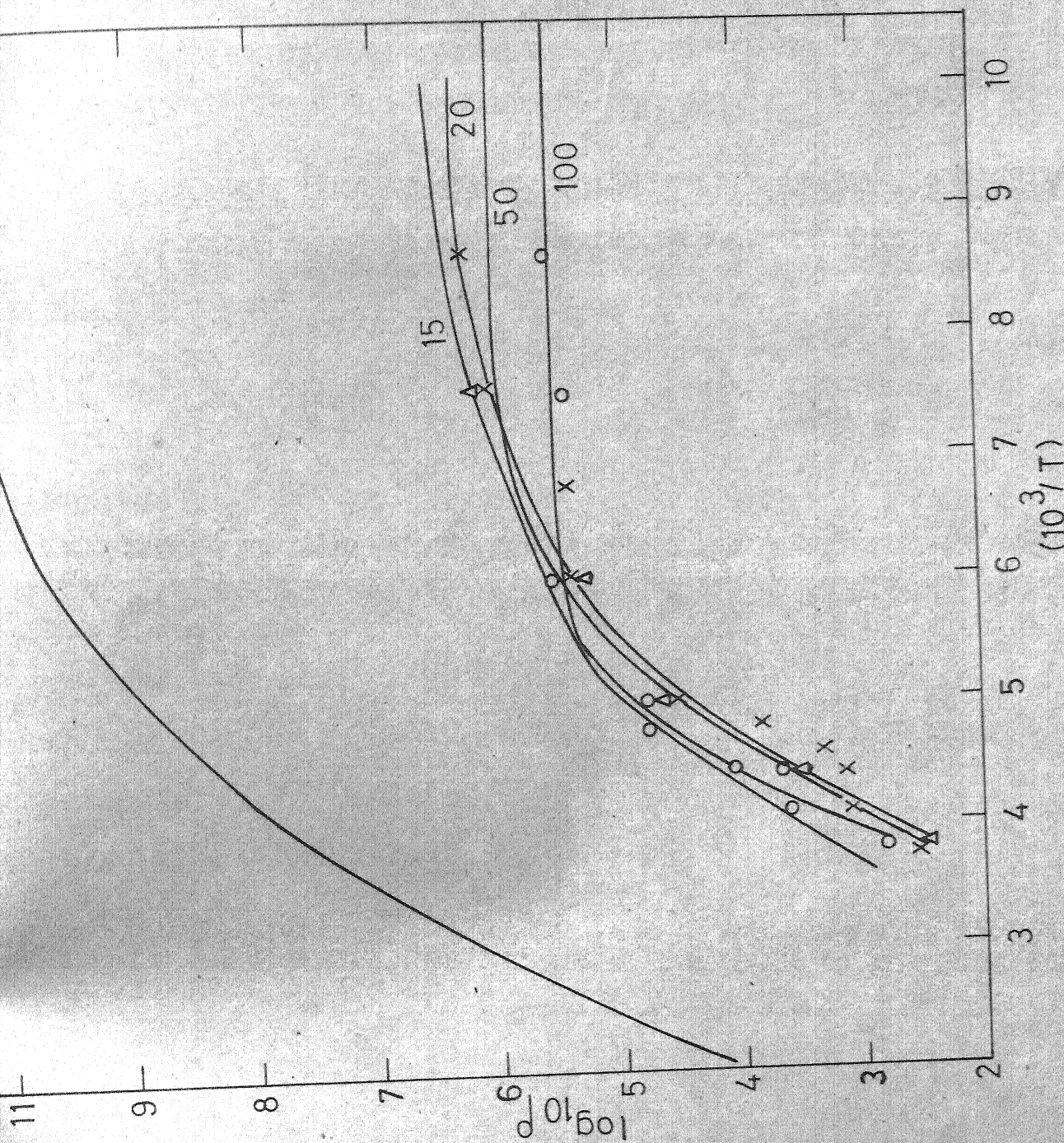


FIG.12 AC CONDUCTIVITY OF GLASS No.4 75V<sub>2</sub>O<sub>5</sub>,15P<sub>2</sub>O<sub>5</sub>,10Ag.



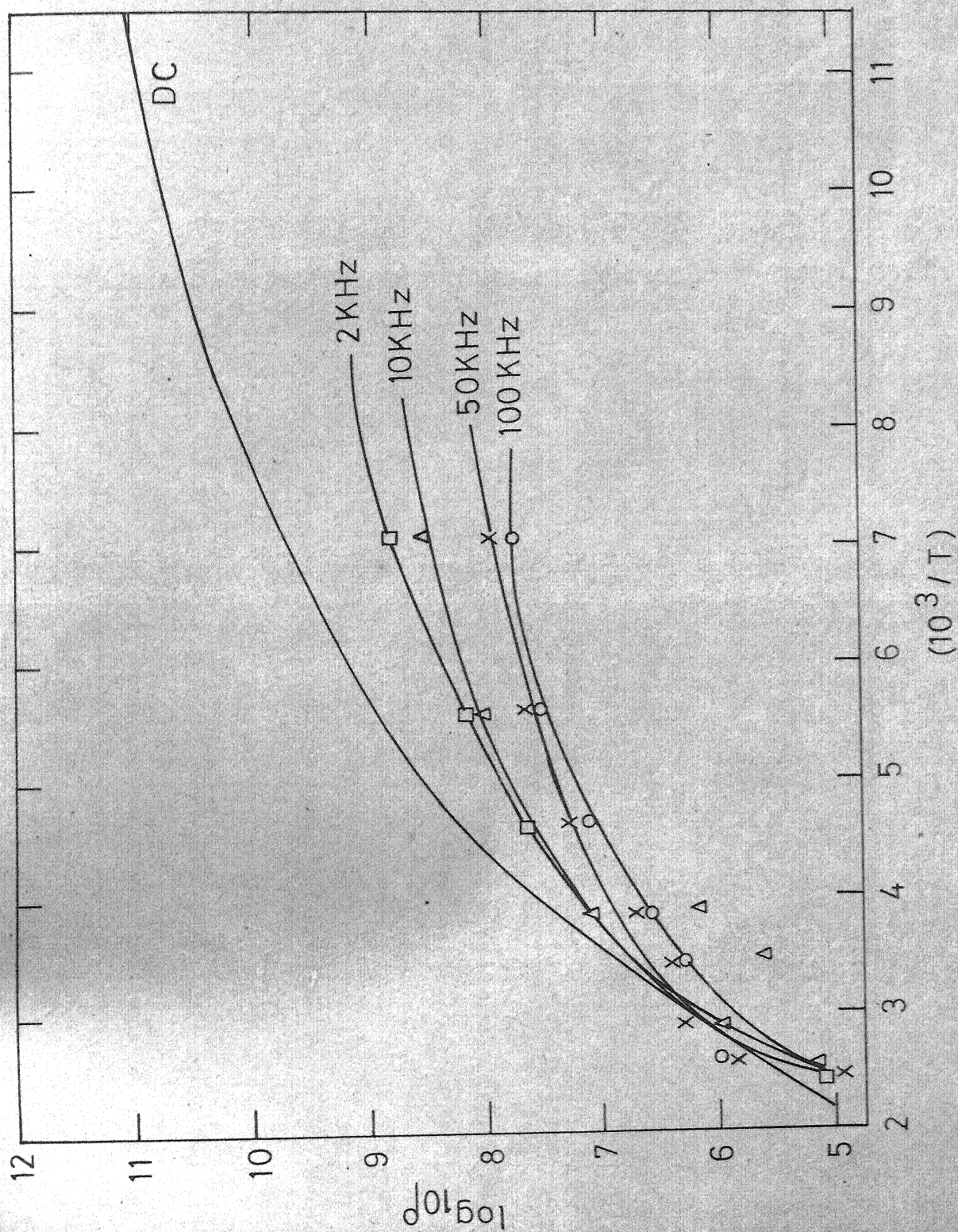


FIG.13 AC CONDUCTIVITY OF GLASS No.7 70V<sub>2</sub>O<sub>5</sub>,15P<sub>2</sub>O<sub>5</sub>,15Bi<sub>2</sub>O<sub>3</sub>



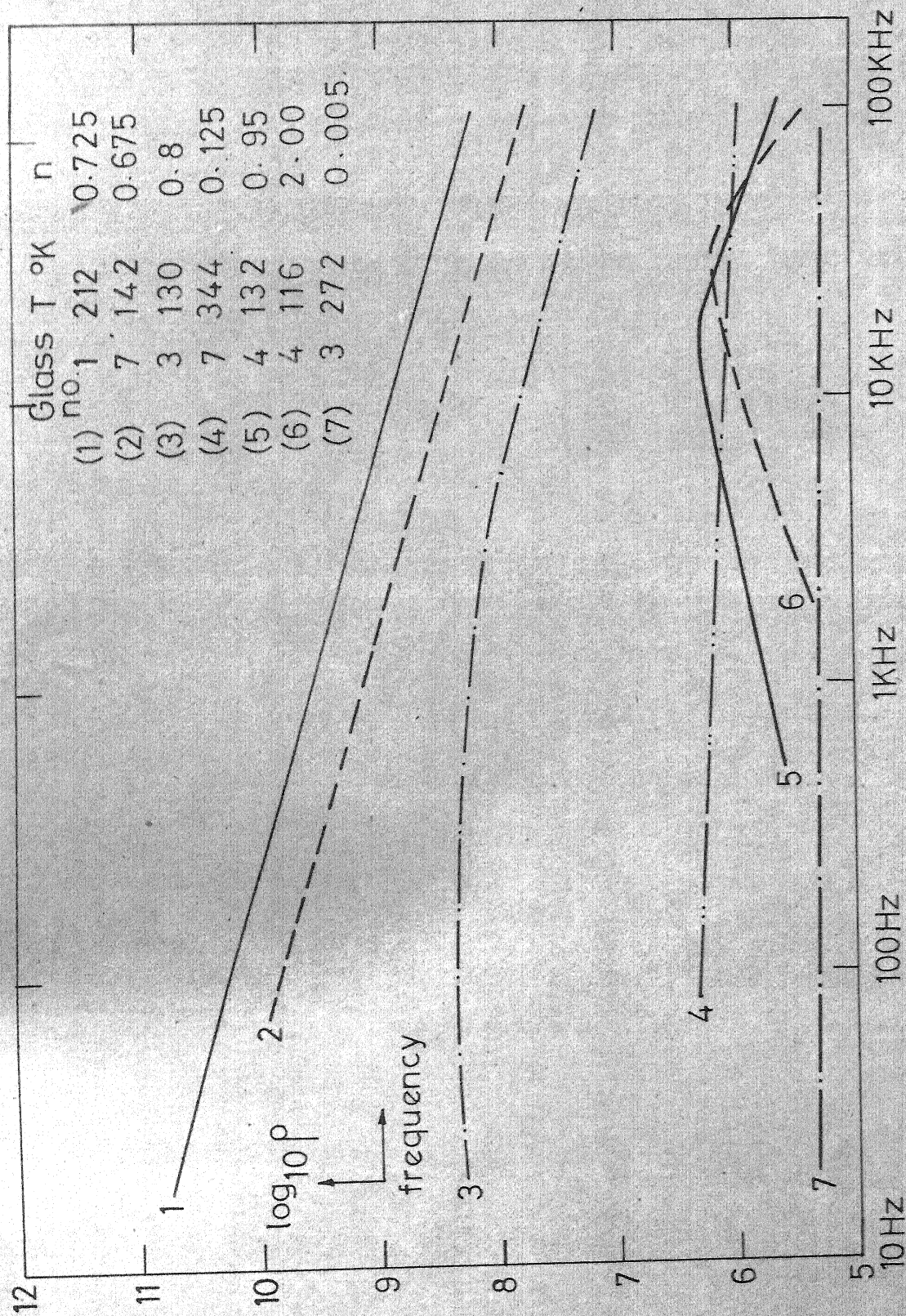


FIG.14 AC CONDUCTIVITY AS A FUNCTION OF FREQUENCY



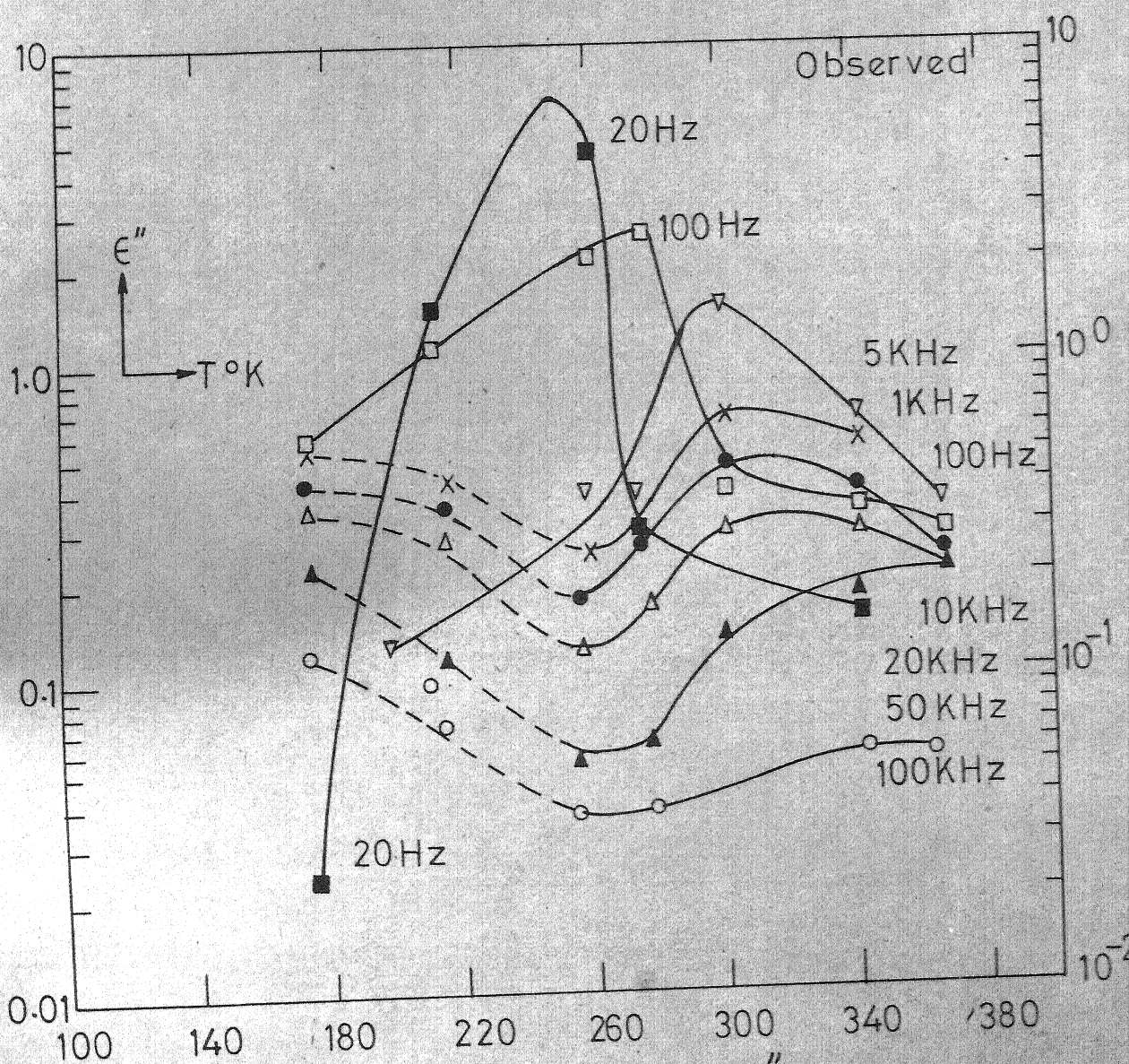
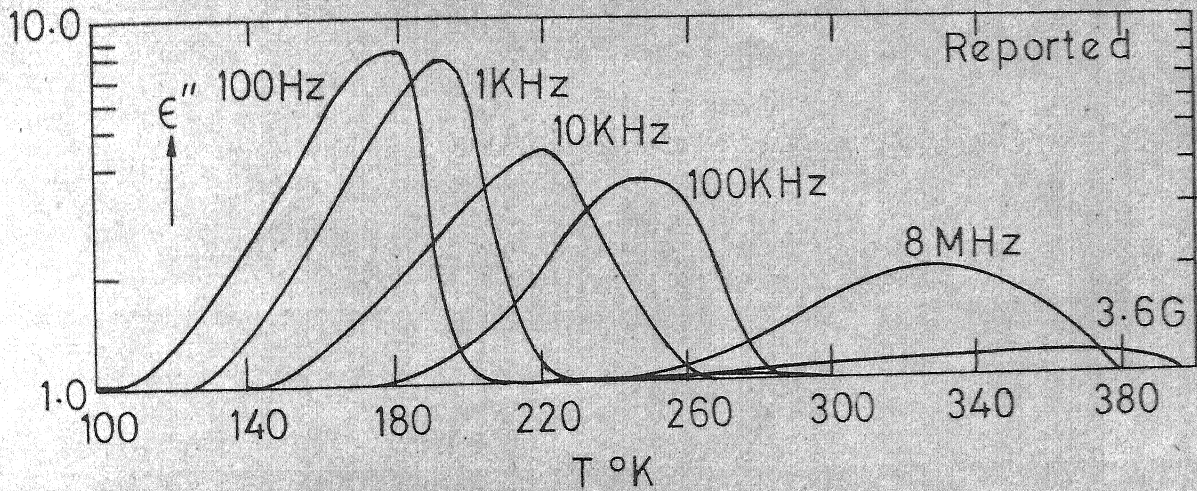


FIG.15 TEMPERATURE VARIATION OF  $\epsilon''$



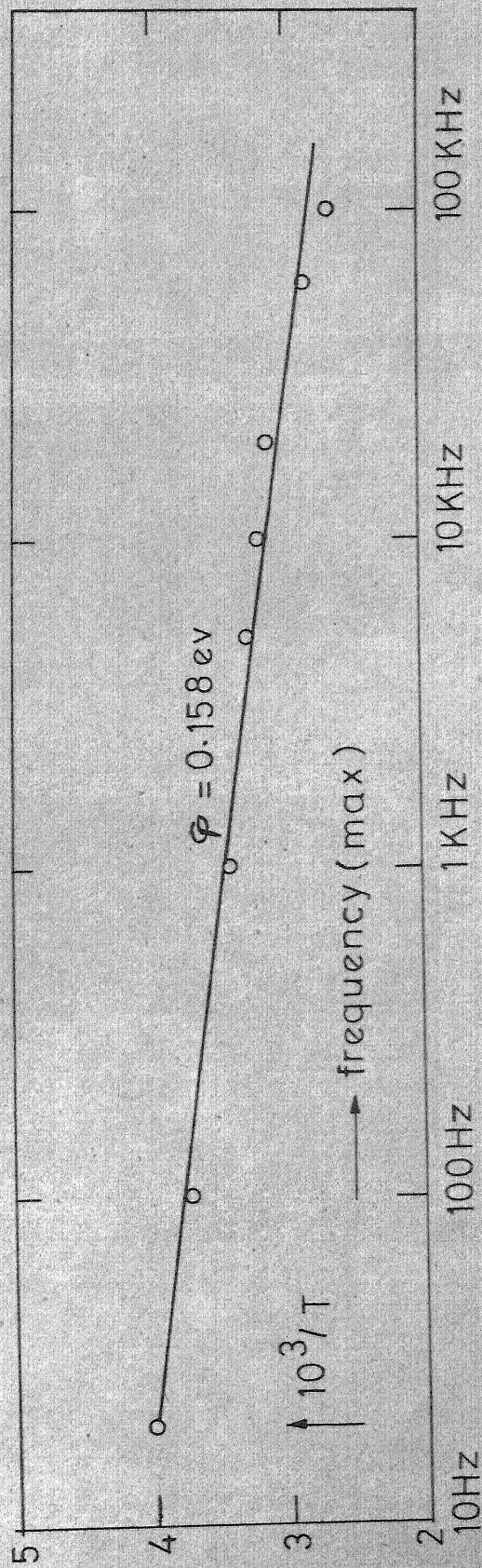
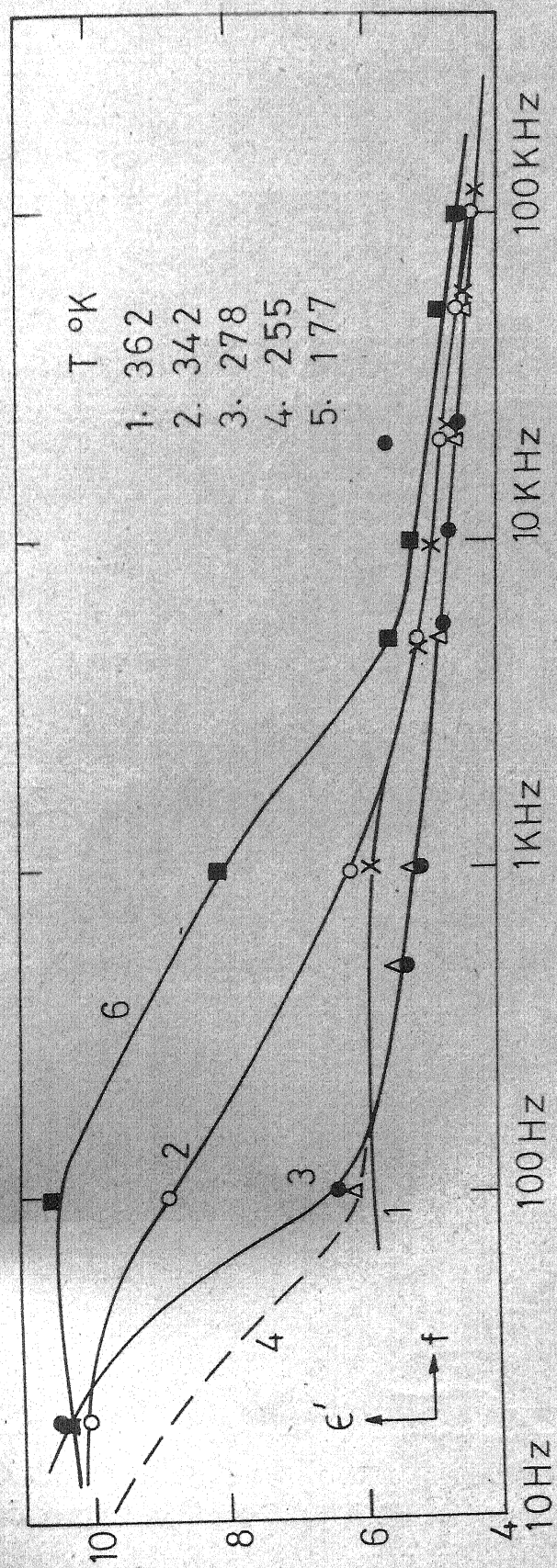


FIG.16 GLASS No.: 1 80V<sub>2</sub>O<sub>5</sub>, 20P<sub>2</sub>O<sub>5</sub>



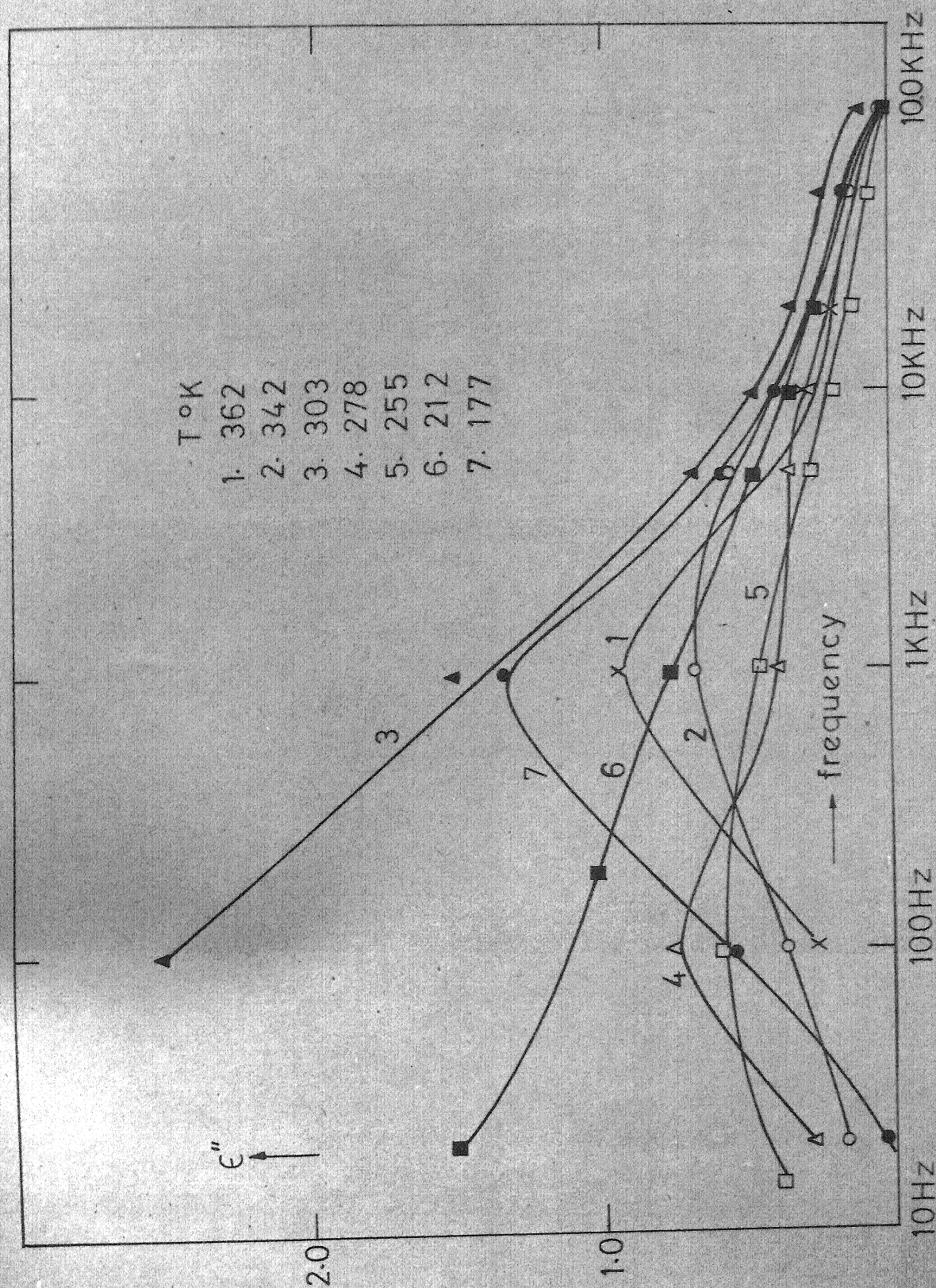


FIG. 17 GLASS No.: 1  $80V_2O_5, 20P_2O_5$



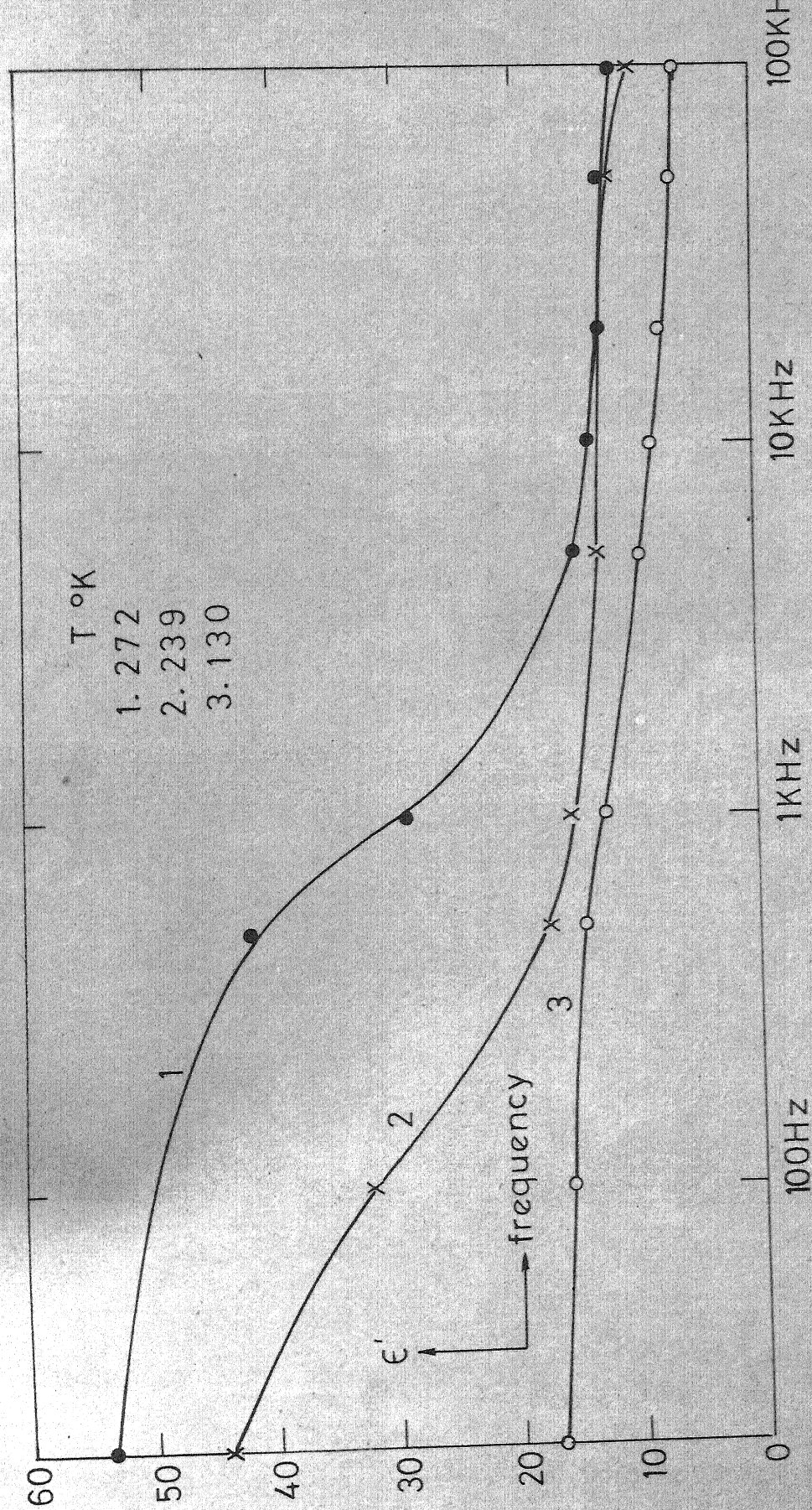


FIG.18 FREQUENCY VARIATION OF  $\epsilon'$  IN GLASS No.3 80V<sub>2</sub>O<sub>5</sub>,15P<sub>2</sub>O<sub>5</sub>,5Ag



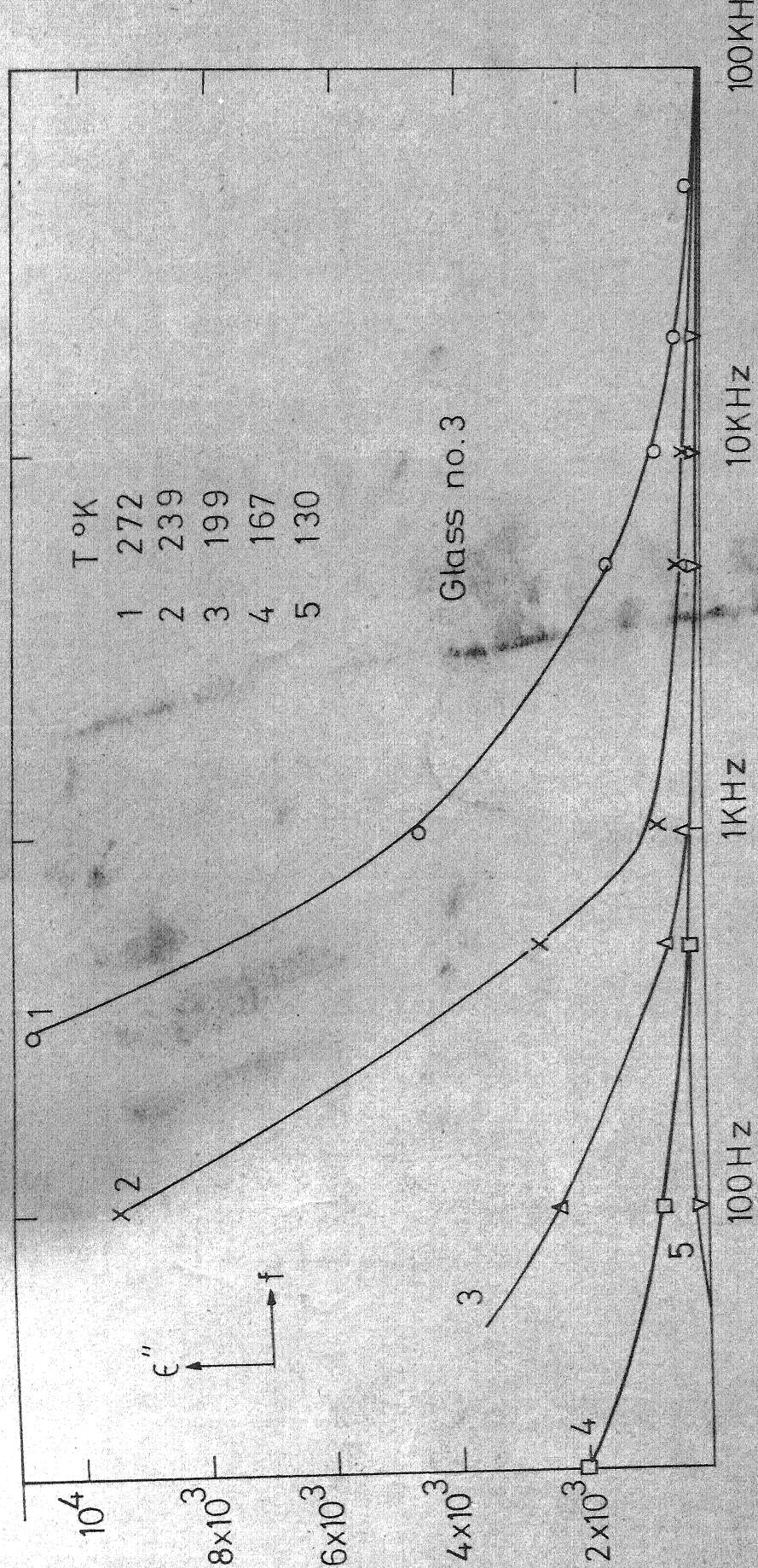


FIG.19 FREQUENCY VARIATION OF  $\epsilon''$ .  $80V_2O_5, 15P_2O_5, 5Ag$



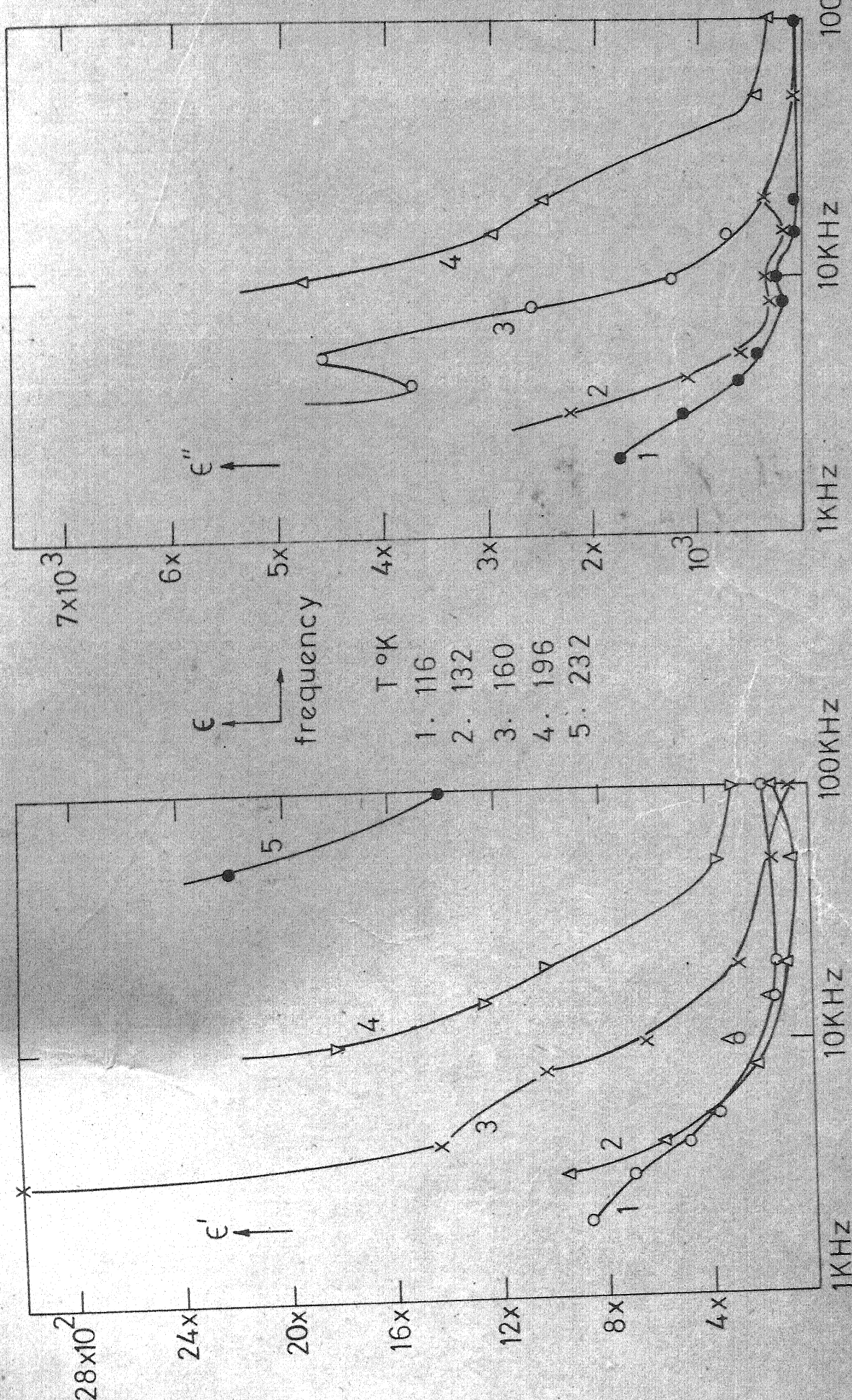


FIG 20 FREQUENCY VARIATION OF  $\epsilon$  IN GLASS No.4 75 V<sub>2</sub>O<sub>5</sub>, 15 P<sub>2</sub>O<sub>5</sub>, 10 Ag.



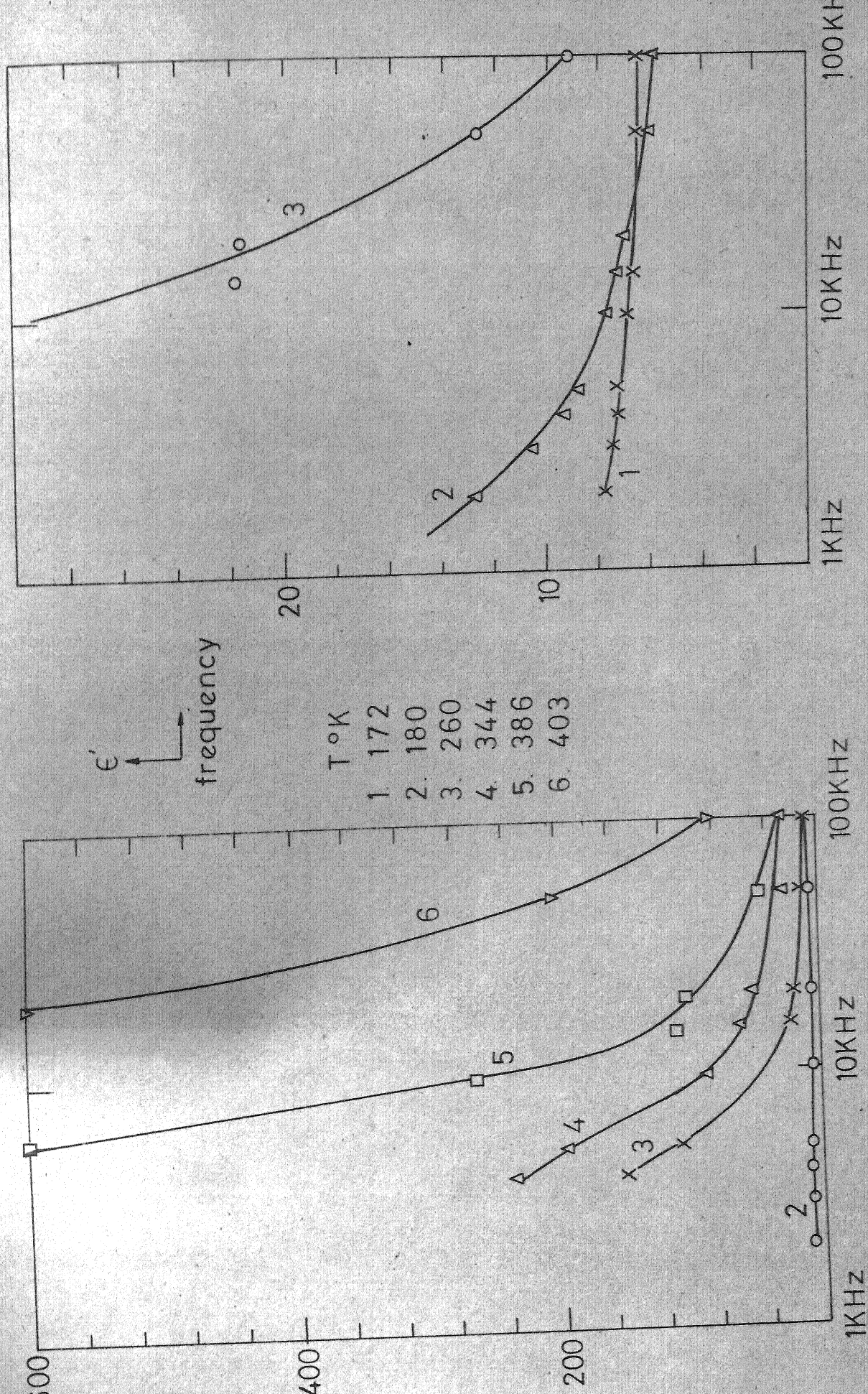


FIG. 21 FREQUENCY VARIATION  $\epsilon'$  IN GLASS No. 7  $70V_2O_5, 15P_2O_5, 15Bi_2O_3$ .



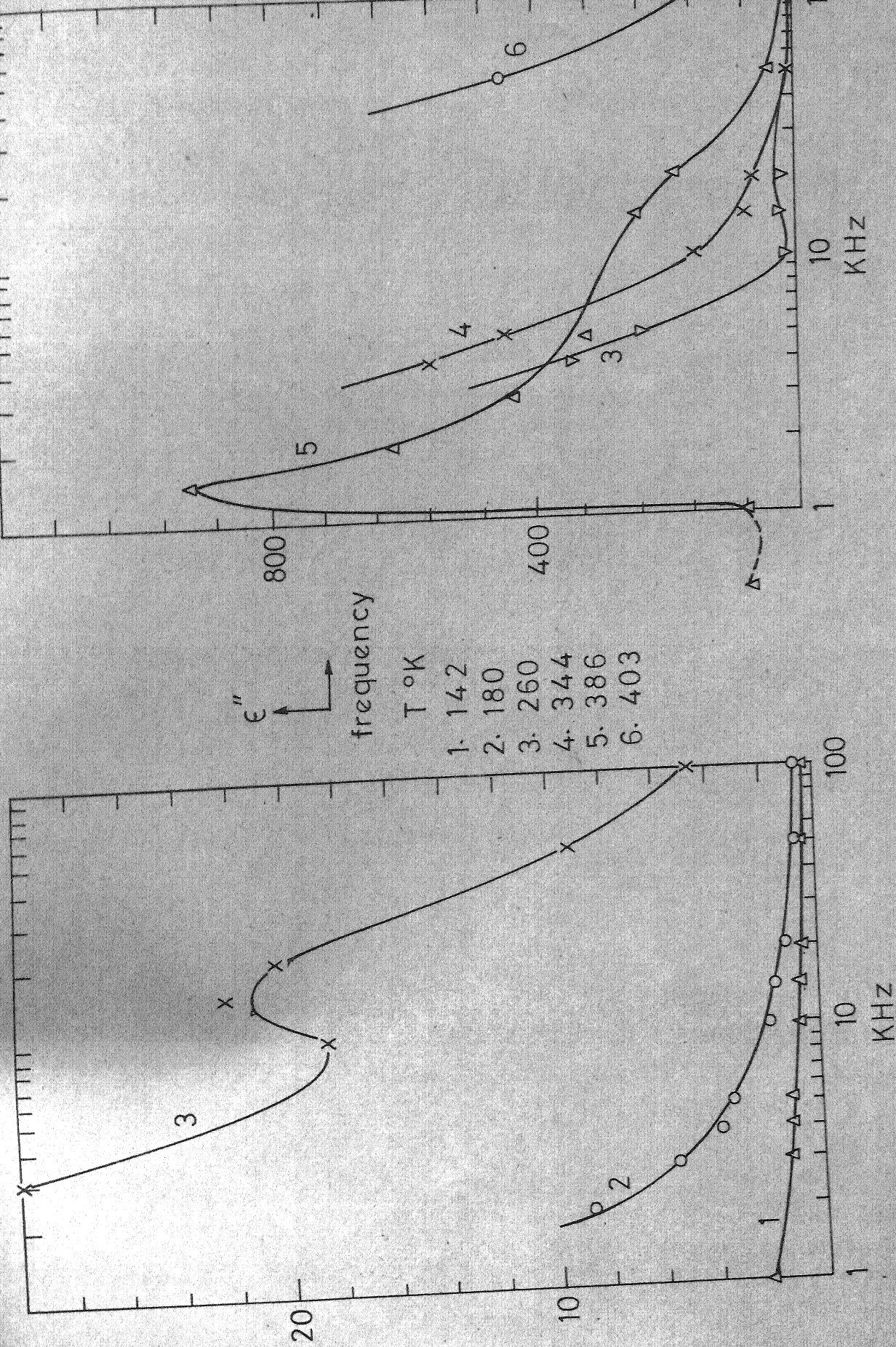


FIG. 22 GLASS No: 7  $70 V_2O_5, 15 P_2V_5, 15 Bi_2O_3$

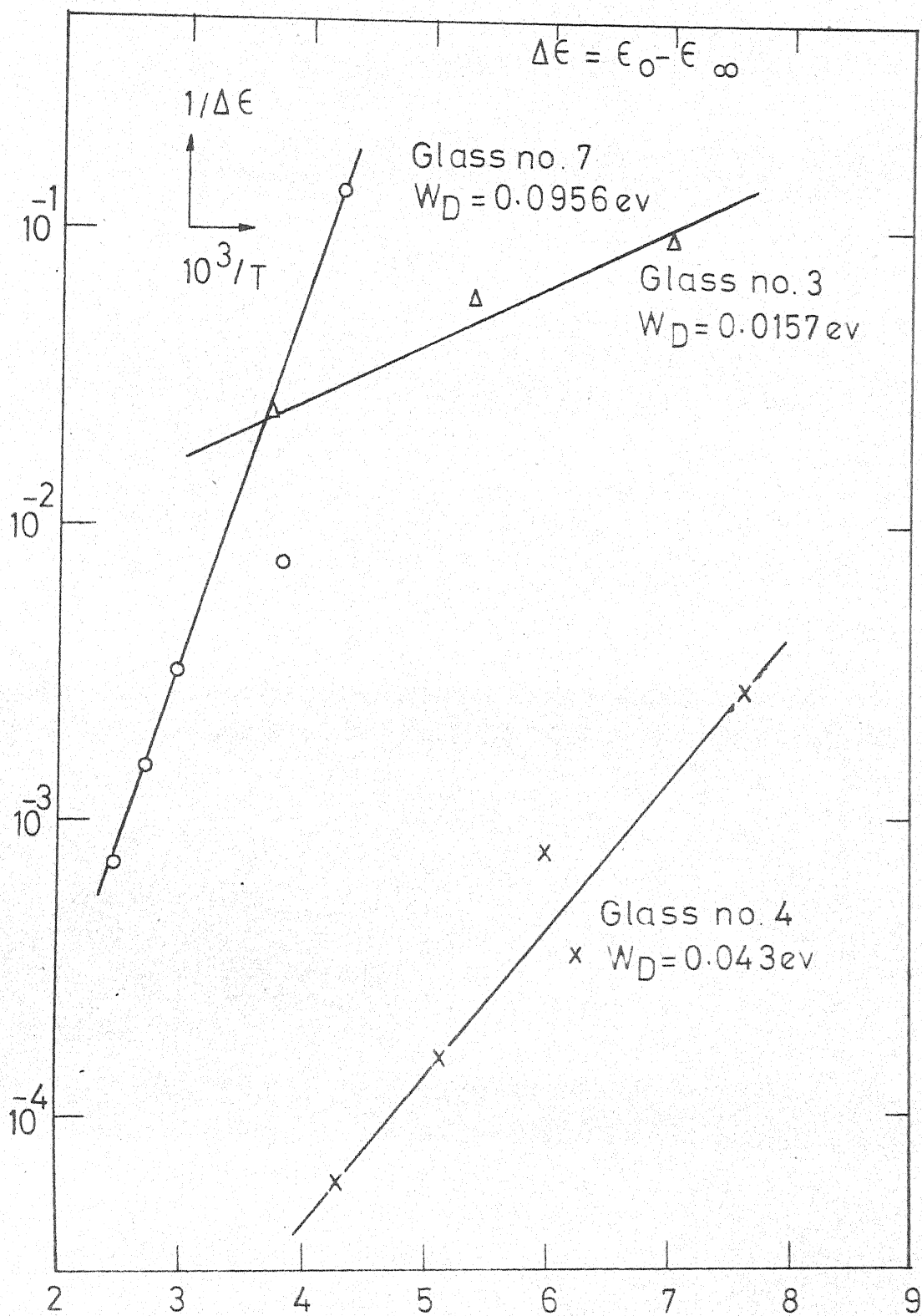


FIG. 23. ACTIVATION ENERGY FROM THE TEMPERATURE VARIATION OF  $\Delta\epsilon'$ .



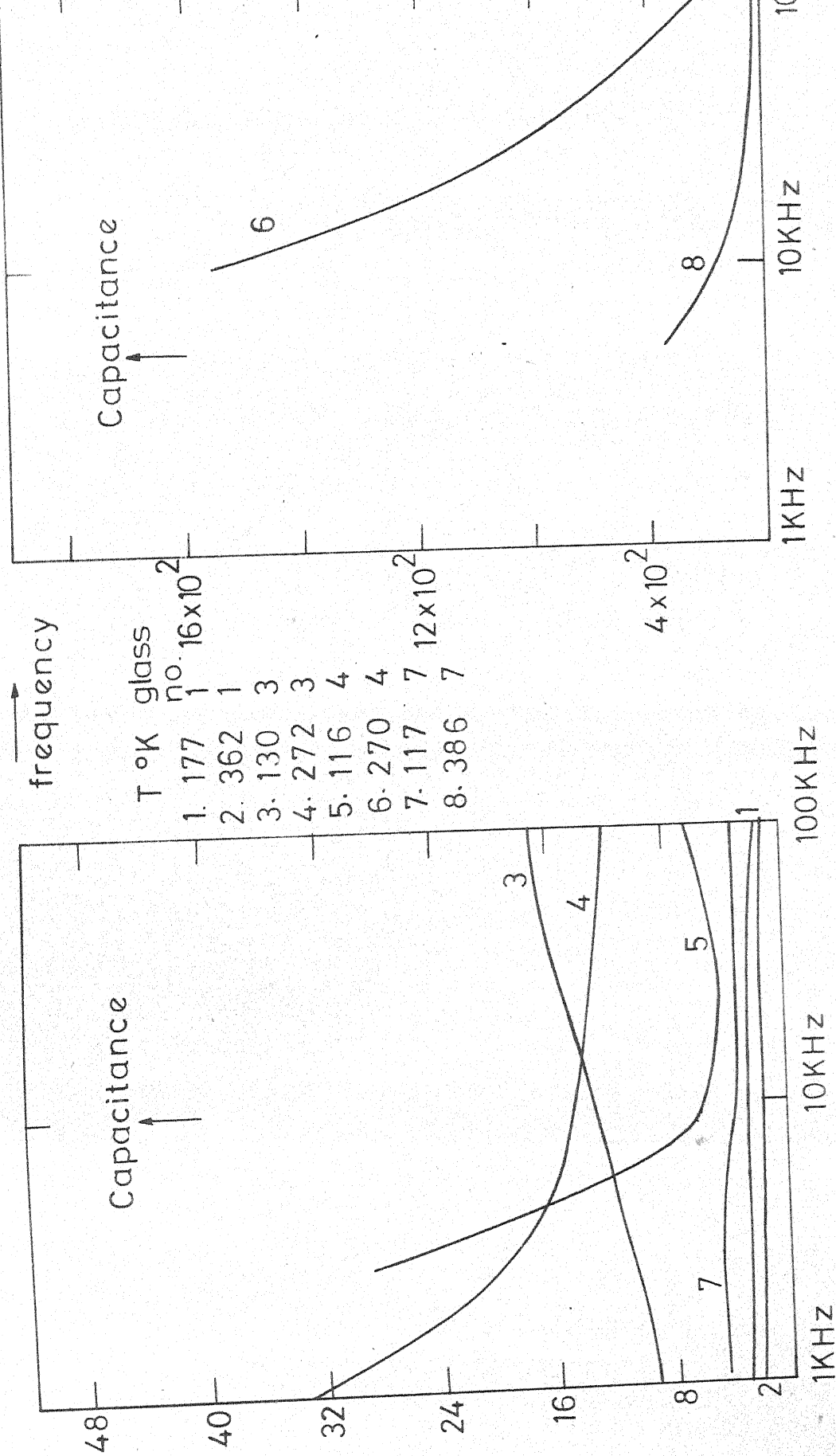


FIG. 24 FREQUENCY VARIATION OF CAPACITANCE

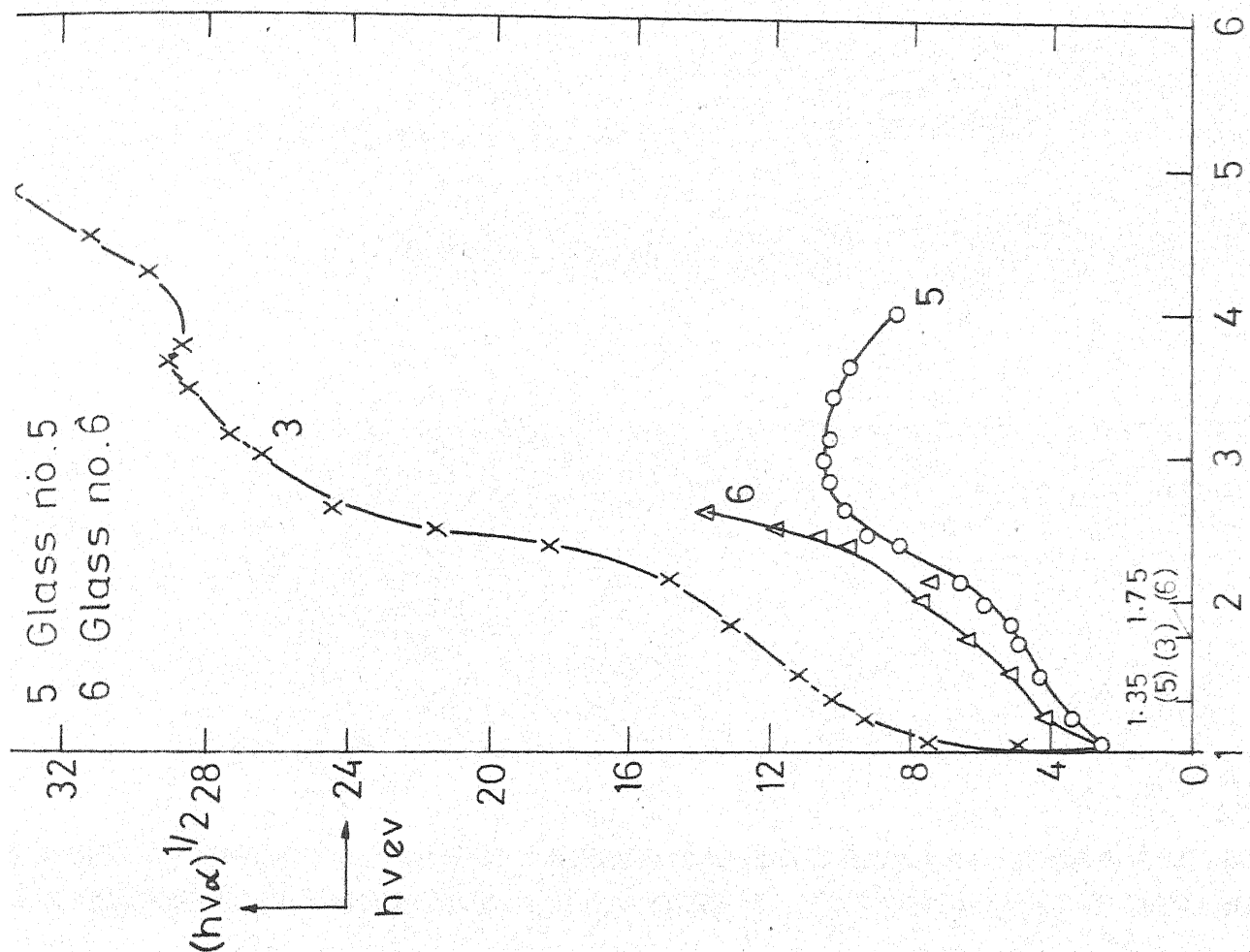
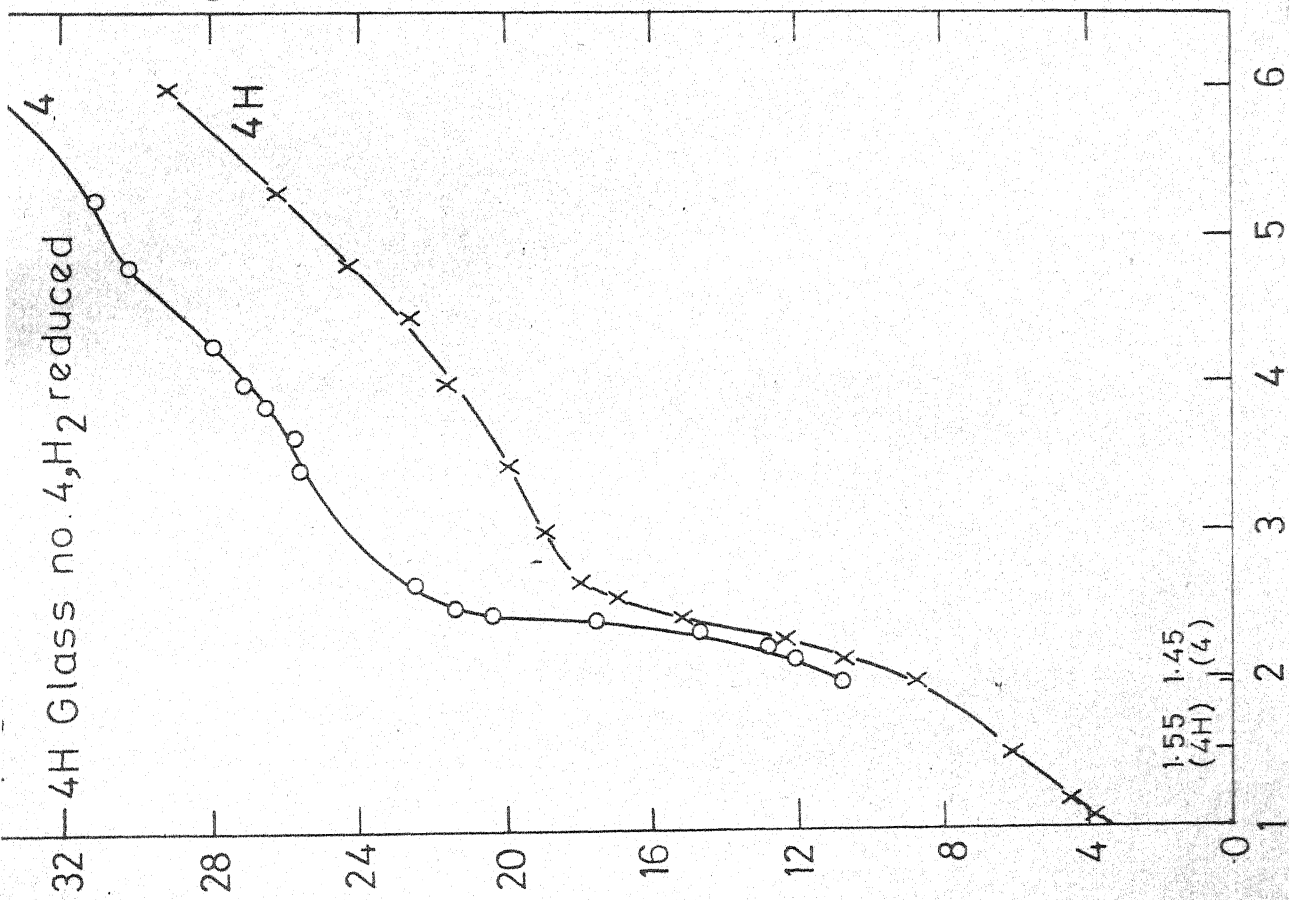


FIG. 25 OPTICAL ABSORPTION edge IN VANADATE GLASSES.

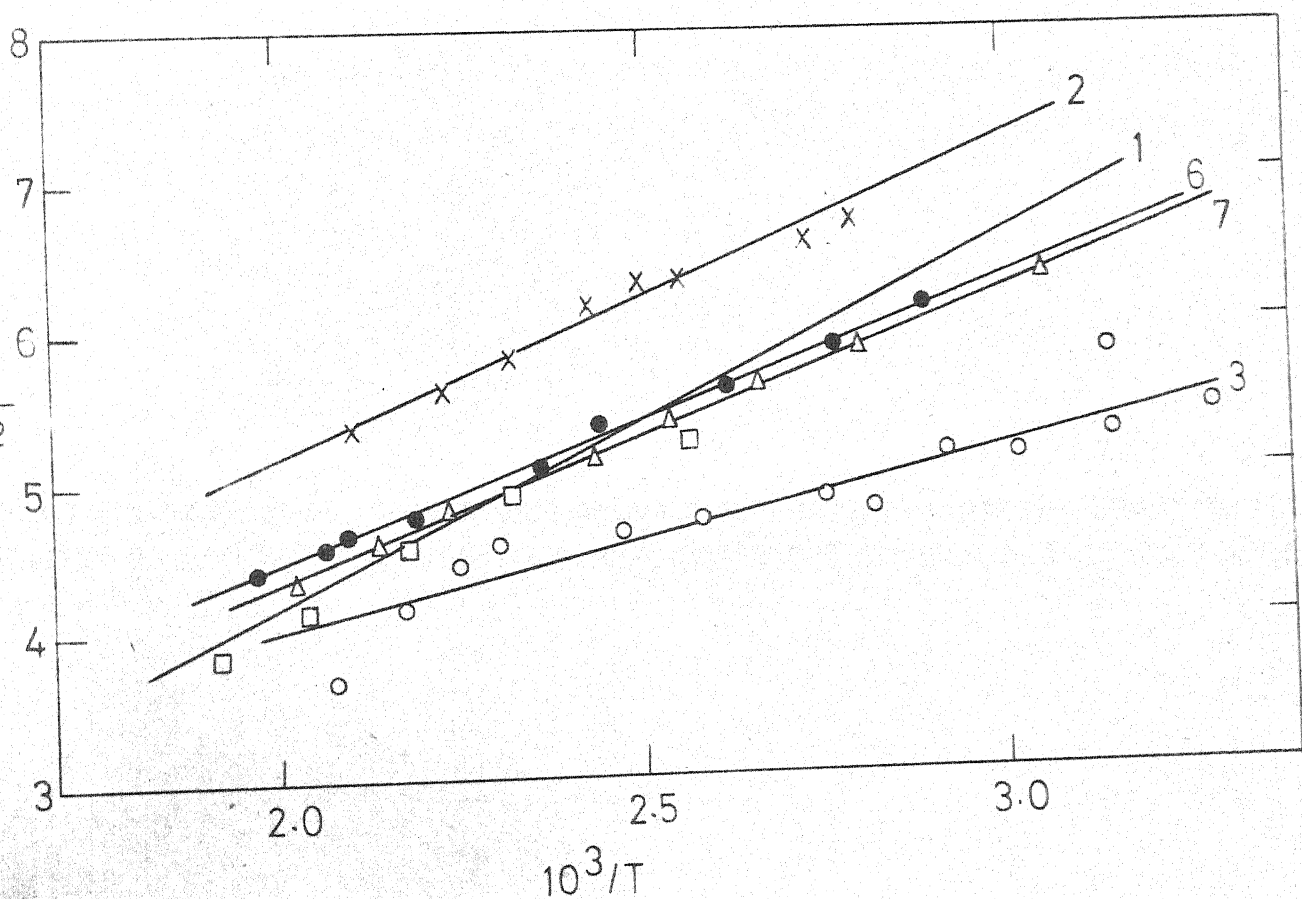
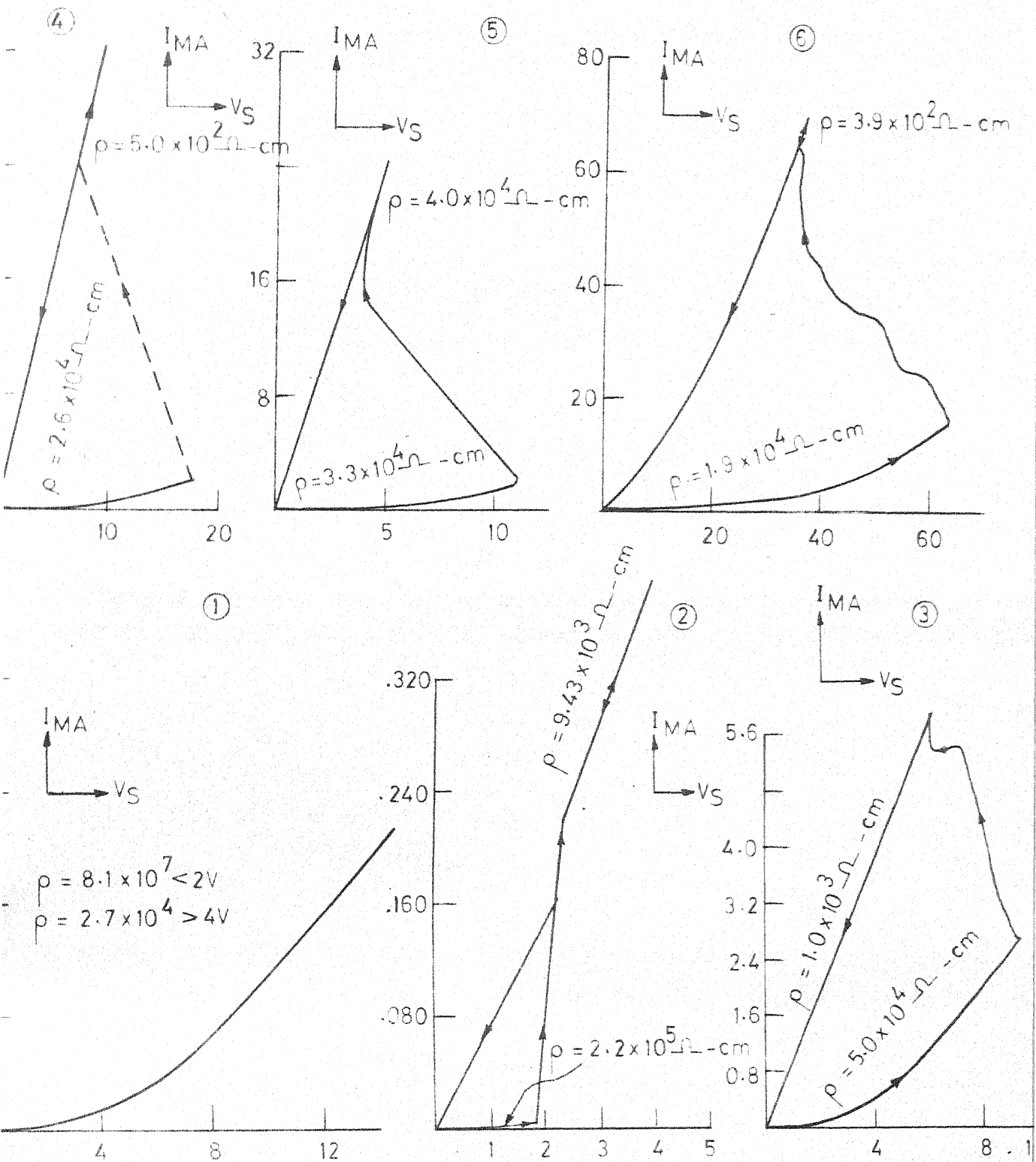
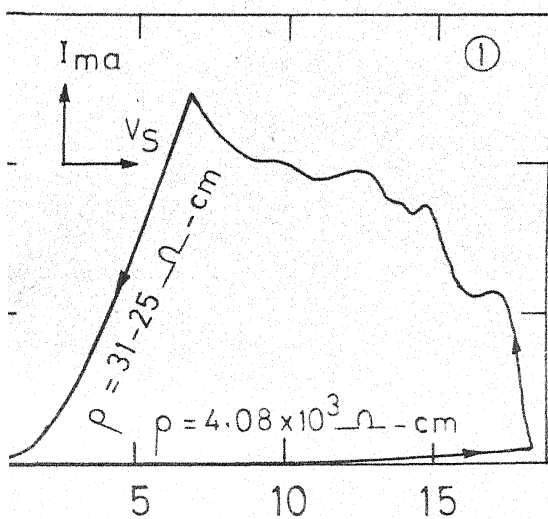
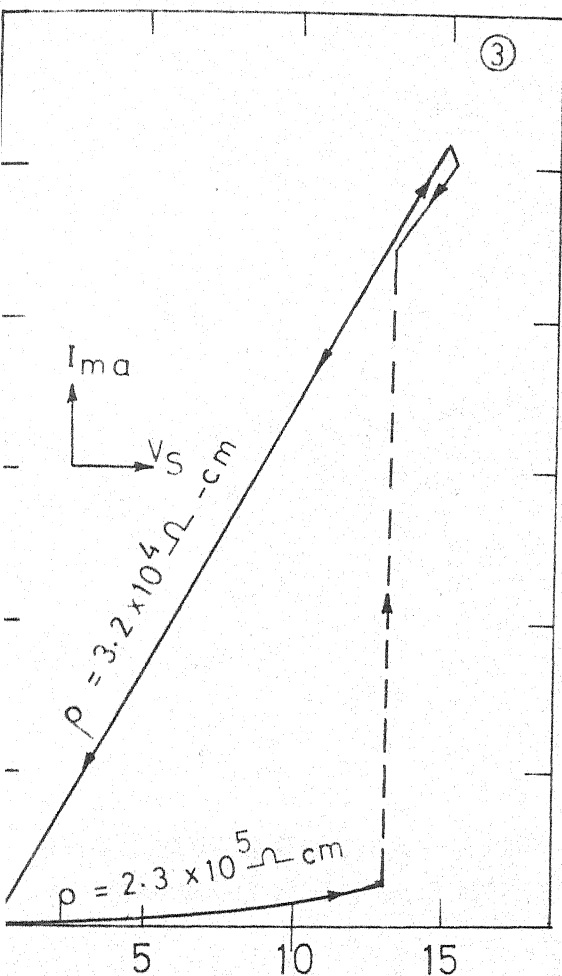


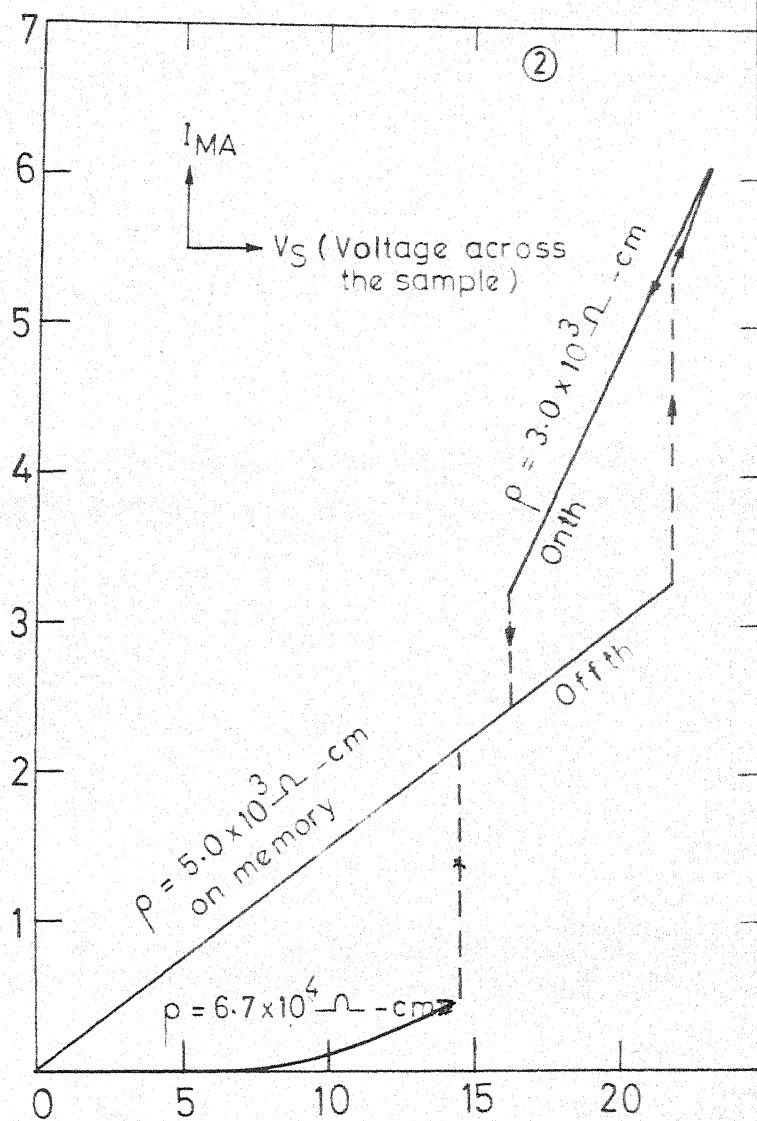
FIG. 26 SURFACE CONDUCTIVITY OF VANDATE GLASSES WITH Ag/Bi ON HYDROGEN REDUCED SURFACE.



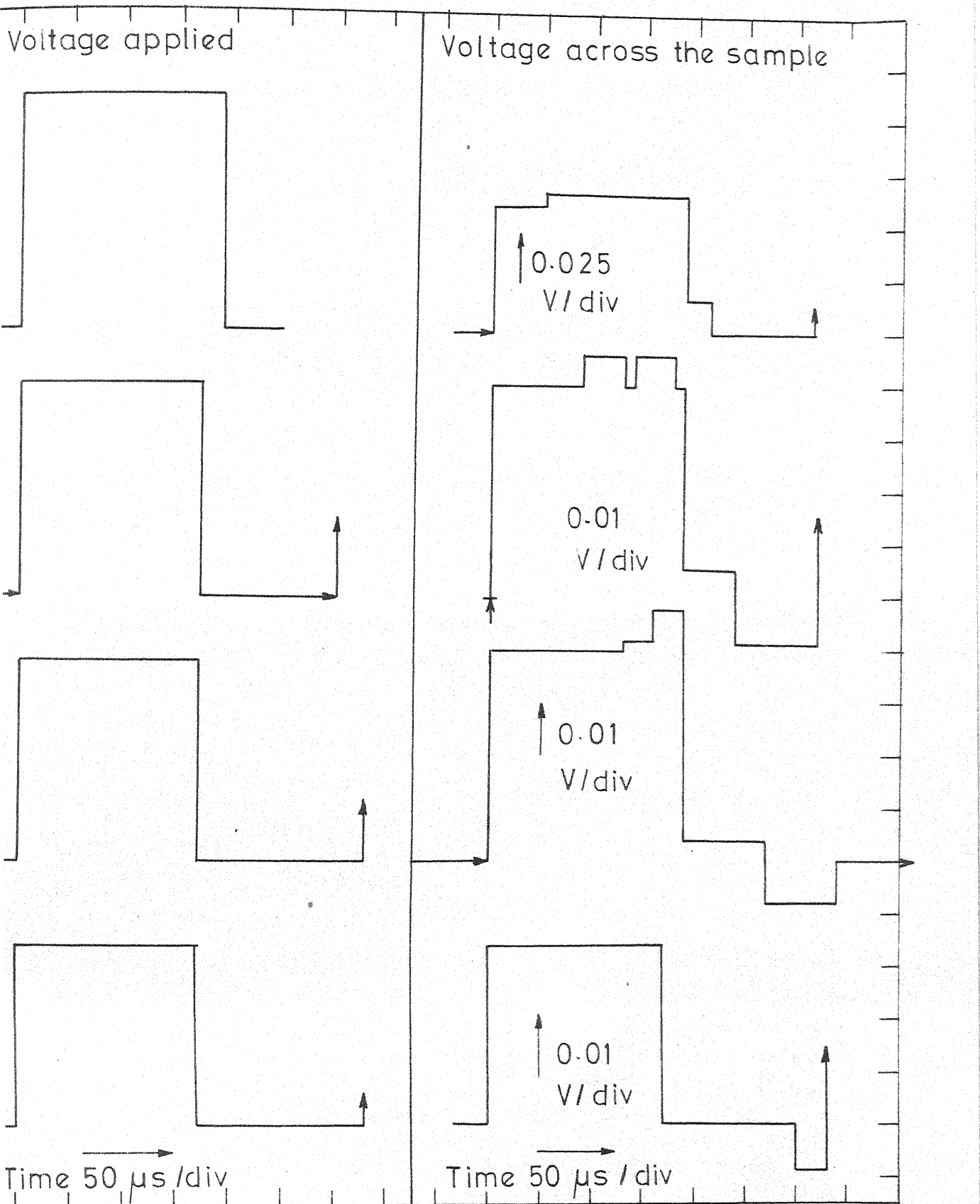
27 SWITCHING IN GLASS No. 4 IN BULK FORM.



	$T^\circ\text{C}$
1	262
2	82
3	32



28 SWITCHING IN GLASS No.7 (Bulk form)



9 THRESHOLD SWITCHING OBSERVED BY THE METHOD OF PUL  
IN GLASS 7 BULK SAMPLE Tempr. =  $30^{\circ}\text{C}$

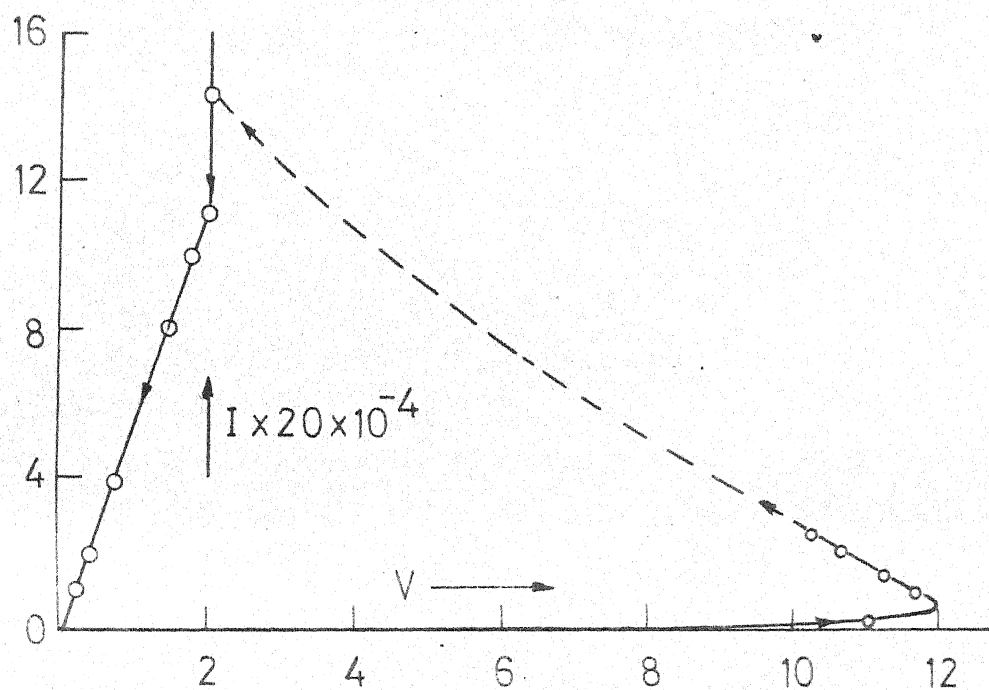
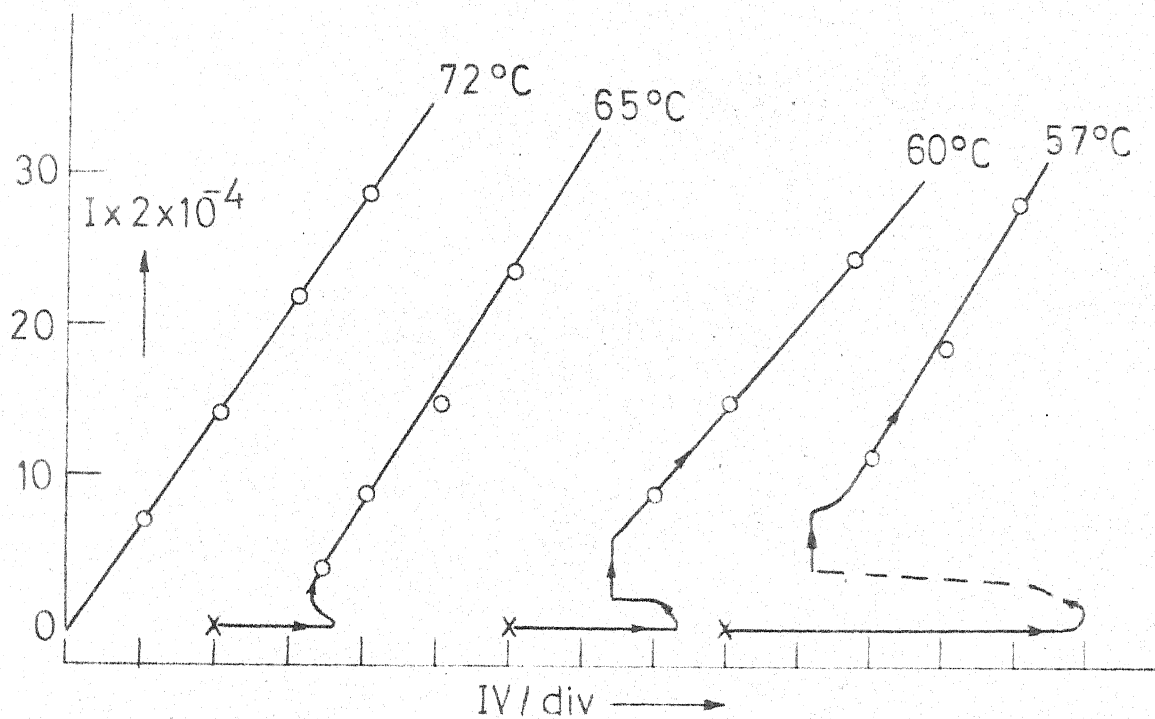
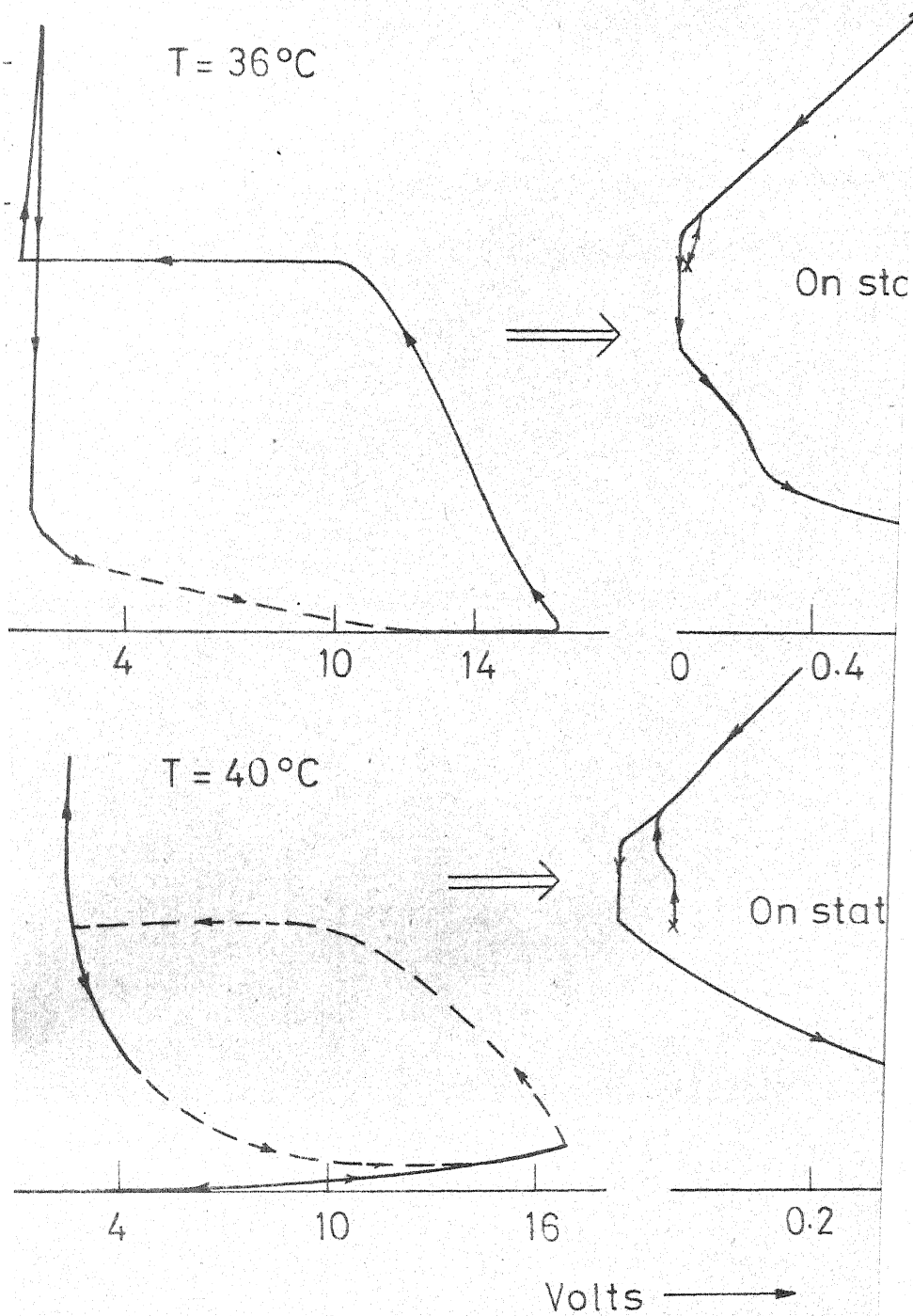


FIG. 30 THRESHOLD SWITCHING IN GLASS No. 5 (Blown film)



31 THRESHOLD SWITCHING WITH NEGA  
No.5(Blown film)



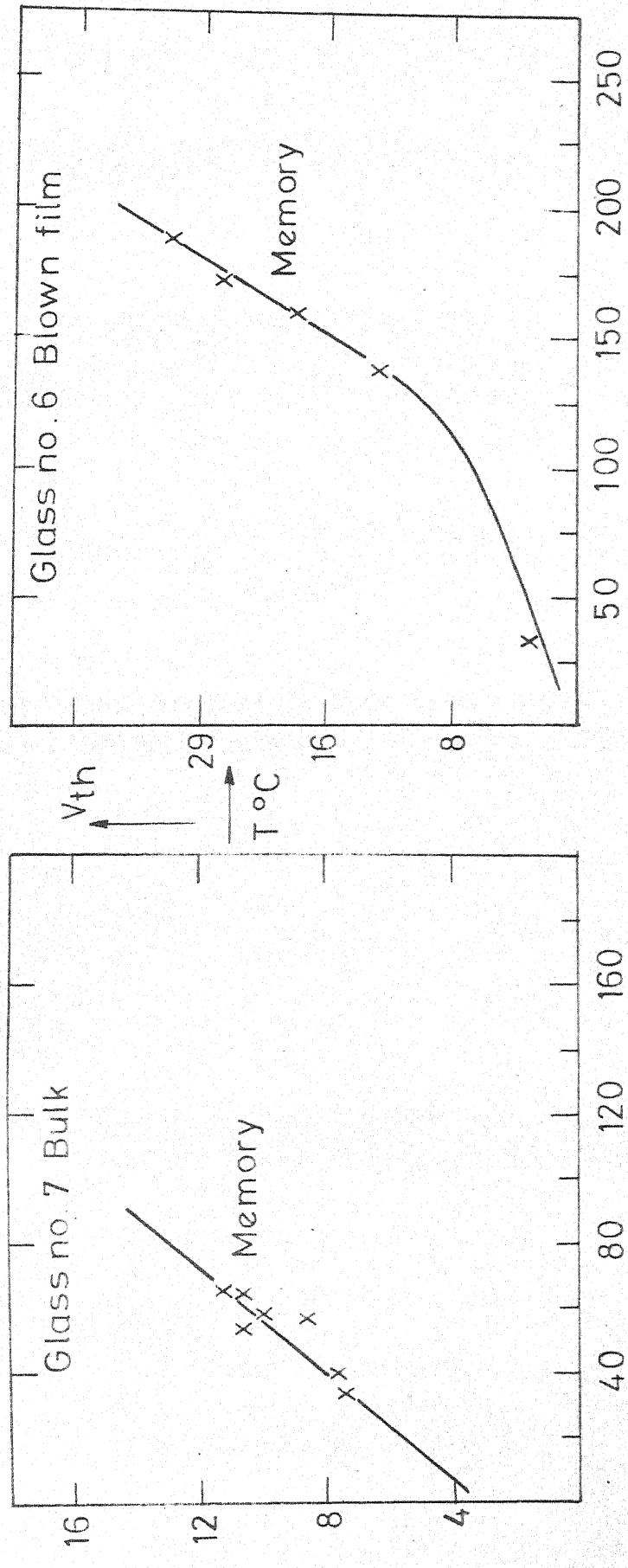
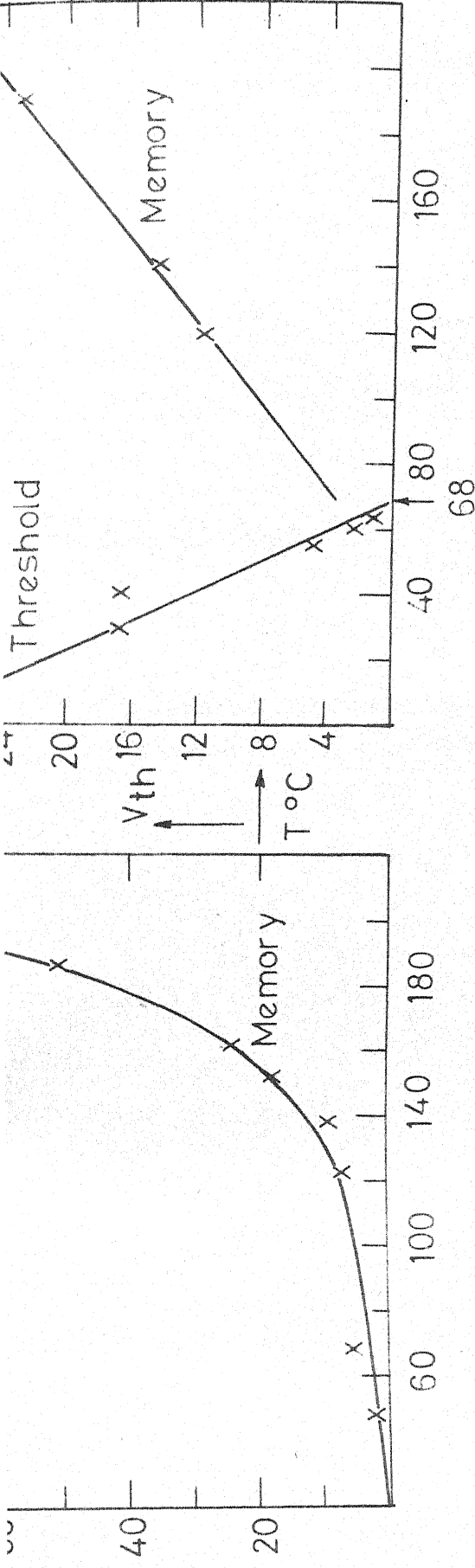


FIG.33 THRESHOLD VOLTAGE AS A FUNCTION OF TEMPERATURE

$10 \times 10^5 \text{ Amps}$

Glass no. 1 with  
Agpaste  $T = 68^\circ\text{C}$

$I$  ↑

$5 \times 10^5 \text{ Amps}$

$V(\text{Volts})$  →

$-5 \times 10^5 \text{ Amps}$

$-10 \times 10^5 \text{ Amps}$

0.4

Glass no.1 with Agpaste  
 $T = 68^\circ\text{C}$

$V_R$  ↑

Time(sec) →

0.08

0.06

0.02

Glass no.1 with Aluminium  
Contact  $T = 18^\circ\text{C}$

$V_R$  ↑

Time(sec) →

20V

Glass no. 3 With  
Agpaste  $T = 200^\circ\text{C}$

$V_R$  ↑

$V(\text{Volts})$  →

0.6

0.4

0.2

Glass no 3 with Agpaste  
 $T = 45^\circ\text{C}$

$V_R$  ↑

Time(sec) →

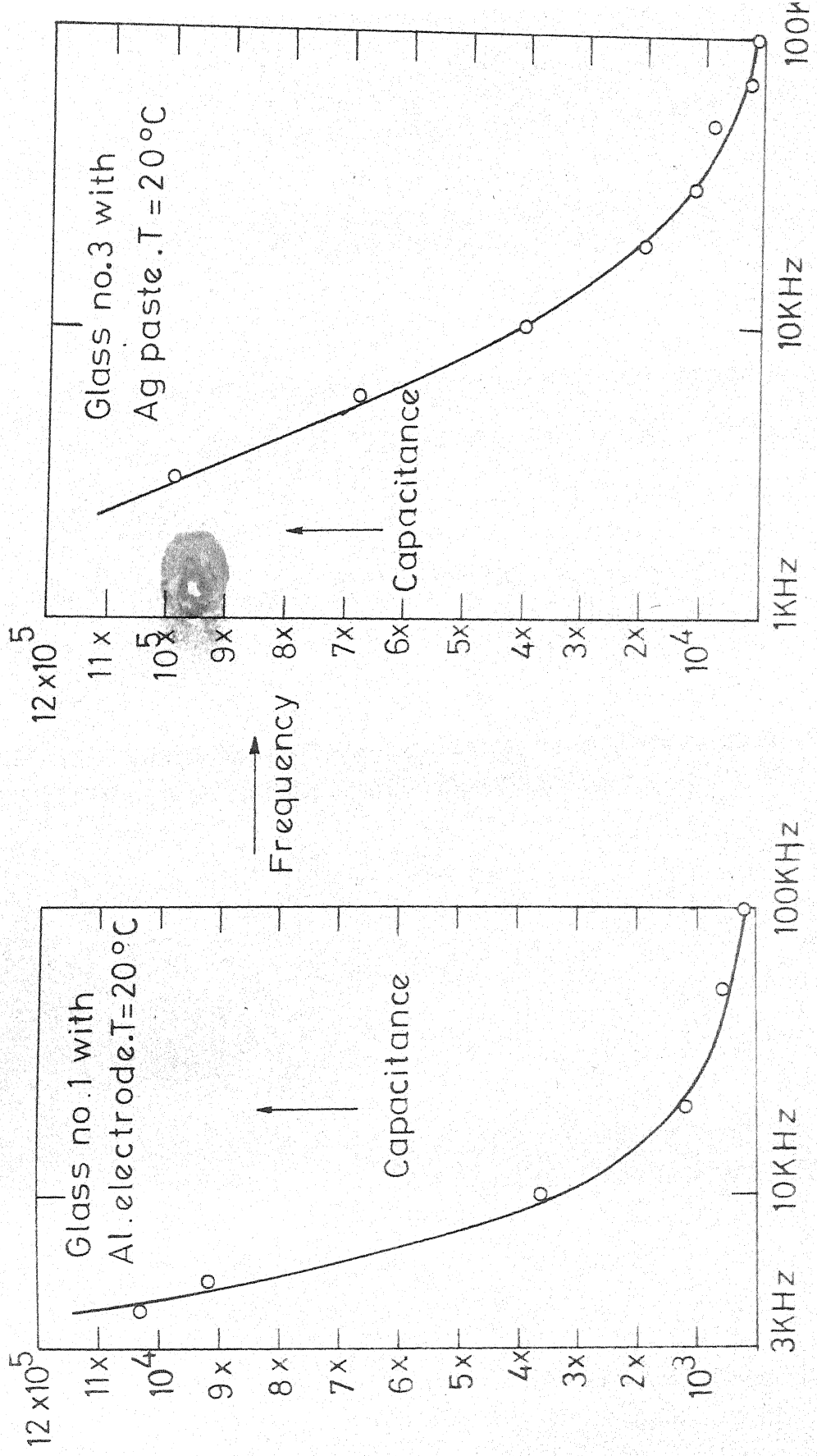


FIG.35 ELECTRODE PROPERTIES OF GLASS No.1 & 3

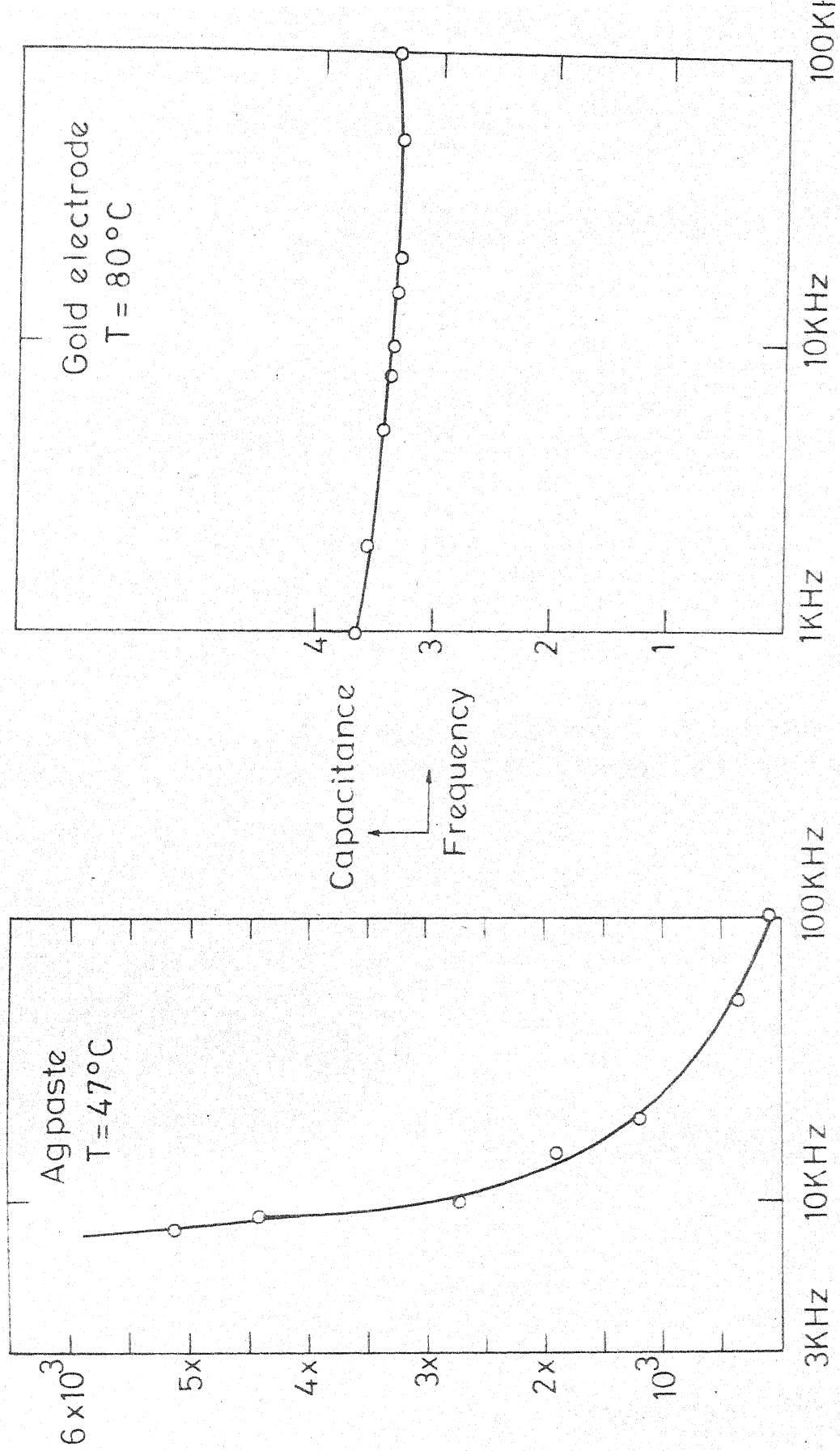


FIG 36 ELECTRODE PROPERTIES OF GLASS No.1

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